

*REMARKS/ARGUMENTS*

In response to the Office Action dated December 29, 2010, Applicants amend their application and request continued examination. In this Amendment no claims are cancelled and new claims 15-18 are added. Accordingly, claims 9-18 are now pending.

*Claim Amendments and New Claims*

After detailed consideration of the commentary in the Office Action dated December 29, 2010, claims 9-14 have been amended to be more specific. In addition, still more specific claims, new claims 15-18, have been added.

Of the formerly examined claims, claim 9 is the sole independent claim. Claim 9 has been clarified to explain that when the organic solvent is placed between the face of the substrate and the polymer pellet, that organic solvent dissolves molecules of the material that is dispersed through, i.e., contained within, the pellet of polymer material. The changed language is intended to avoid the misinterpretation of the claim language, discussed in greater detail below, that is the basis of nearly all of the formality rejections. In that misinterpretation, the Examiner has repeatedly insisted that the invention is directed to and requires the extraction of every molecule of a material that is dispersed throughout the polymer pellet, from that polymer pellet. There is no such description in the patent application and, as explained below, one of the important achievements of the invention is rapid evaluation of a plastic or polymer to determine whether it contains a particular material in a minute quantity. That result can only be achieved if fewer than all of the molecules of the material dispersed in the pellet is removed in a dissolution process. Therefore, it is ironic that the Examiner has insisted on a totally inverted interpretation and misunderstanding of the invention and what is disclosed and claimed in the patent application.

The invention is of substantial importance in quickly evaluating plastics used in electronic components to determine if the plastics contain particular materials, such as

certain brominated flame retardants that are prohibited according to environmental regulations of the European Union. Applicants agree that prior methods of analysis, such as those cited by the Examiner, in which every molecule, or essentially every molecule, of a dispersed material is removed from a sample of a plastic material require many hours. Those processes are directed to providing an ultra-precise analysis of that plastic pellet sample. An important advance of the invention is the rapid determination as to the presence or absence of particular materials dispersed in plastics, such as the prohibited flame retardant constituent just mentioned. The identification, and even a quantitative analysis, of those constituents does not require the extraction of every molecule of the constituent from a polymer pellet. That pellet, of course, represents a sample of a larger assembly or component.

The claims that depend from claim 9, namely claims 10-14 have been amended merely to conform to the amendment of claim 9. These amendments include improved precision in certain words and terms so that, for example, the word “extract” and the phrase “minute content” no longer appears within any of those claims. Likewise, those terms do not appear in the newly added claims.

As pointed in the previous Reply, independent claim 9, like new independent claim 17, is supported at least by Example 5, which is described at pages 20-22 of the patent application as filed. Claim 10 is supported by Example 9, as is new claim 16. That Example 9 is described at pages 26 and 27 of the patent application as filed. Example 7 of the patent application, described at page 24 of the patent application provides support to claims 11 and 12. Claims 13 and 14 are supported by Example 8 which is described at pages 25 and 26 of the patent application as filed, not the substitute specification.

The newly added claims, claims 15-18, are directly taken from specific examples of the invention that are described in the patent application as filed. The Examiner is invited to compare, directly, those claims with the indicated examples that provide support for the claims. Claim 15 is supported by Example 6; claim 16 is supported by Example 9; claim 17 is supported by Example 5; and claim 18 is

supported by Example 8. These claims are relatively specific and describe particular flame retardants dispersed within pellets of specific polymers and the particular organic solvents employed to dissolve either the polymer and its constituent flame retardant or to dissolve the flame retardant itself. As a result of the dissolution process, some of the flame retardant is left on the silver face of the substrate that supports, during the dissolution, the pellet and the solvent. The residue, i.e., condensate, that is left on the silver face of the substrate is analyzed by time-of-flight, secondary ion mass spectrometry (ToF/SIMS). The results of that ToF/SIMS analysis, with the assistance of measurements of similar plastics with known concentrations of the flame retardants, reveal the concentration of the flame retardant in the respective polymers. The patent application clearly describes, in connection with the cited examples, the establishment of those standard materials. The concentrations of the flame retardants in the standard, i.e., reference, materials may be determined by, for example, gas chromatography-mass spectrometry (GC/MS) to confirm the correlation of the ToF/SIMS measurements of the samples that are otherwise compared to spectrographic analysis of the reference pellets. As explained below, there is a linear relationship between the results obtained in the invention using ToF/SIMS and the results obtained by GC/MS. That linear relationship was determined as part of the development of the present invention.

The amended, previously examined claims and all of the newly added claims are clearly supported by the patent application as filed, and no new matter is added by either the amendments or the addition of the new claims.

#### *Rejections Pursuant to 35 USC 112, First Paragraph and Responses*

In the Office Action dated December 29, 2010, the Examiner renewed her assertion that the specification fails to provide a written description, as required by the first paragraph of 35 USC 112, of the invention. In quoting that statutory section at page 2 of the Office Action, the Examiner also included that portion of the statutory paragraph that refers to enablement. The reference to the same statutory paragraph, under

the heading on page 3 referring to that paragraph, again seems to refer to the written description requirement. As best understood, the lengthy commentary extending through page 9 of the twelve pages of the commentary of the Office Action seem to invoke, but mix together, the distinct requirements of the first paragraph of 35 USC 112 concerning written description and enablement. Although perhaps inefficient, Applicants separately respond to these two distinct statutory requirements.

Response to the Lack of Written Description Rejection. The burdens placed upon an examiner in making a proper rejection for lack of written description, while discussed in bewildering detail in MPEP 2163, are more succinctly stated at MPEP 2163.04. There, two factual findings are identified as essential to supporting such a rejection.

“The findings should:

(A) Identify the claim limitation(s) at issue; and

(B) Establish a *prima facie* case by providing reasons why a person skilled in the art at the time the application was filed would not have recognized that the inventor was in possession of the inventor *as claimed*... .”  
[Emphasis added.]

The lengthy narrative of the Office Action does not clearly set forth in numbered paragraphs, or the like, an identification of the claim limitations at issue consistent with the cited section of the MPEP. Thus, Applicants have attempted to identify in the narrative of the Office Action what claim language the Examiner has relied upon in citing various prior art publications as support for the *prima facie* case of part (B) of MPEP 2163.04.

Since there is no specifically cited claim language in this rejection, Applicants have to infer from the commentary of the Office Action what claim language provides the basis of the rejection. It appears that the Examiner has stated two different bases for the rejection at pages 2 and 3 of the Office Action for the written description requirement rejection. According to the last paragraph that begins at page 2 of the Office Action, the Examiner asks, “If the additives are evenly spread through the bulk of the polymer sample, how is it possible *to completely extract* the additives from the sample by contacting only one surface of the sample with the solution?” [Emphasis

added.] Applicants presume that the question is a statement that it is the Examiner's view that the claimed subject matter that is the subject of the written description requirement describes completely extracting an additive from a sample.

As in responding to the previous Office Actions, Applicants readily agree that there is no supporting description for the subject matter that the Examiner presumes is claimed. However, the rejection is erroneous because the Examiner's presumption as to what is being claimed is incorrect. The Examiner has continually insisted that the claims require the complete extraction of the additive, for example, the flame retardant from the polymer pellet. The claims presented in the previous Reply and the claims presented here *do not* require or even imply that in the claimed process all of the additive is removed from the pellet. If the Examiner continues to disagree, Applicants respectfully request the Examiner to direct attention to the particular language in the rejected claims that states that the claimed method requires removal of all of the additive from the pellet.

What the actual claimed subject matter is, with respect to the independent claims now pending, is that the organic solvent dissolves molecules of the material contained in a minute amount in the pellet. Claim 9 describes dissolving molecule of material contained in the pellet. Claim 15 describes dissolving the polystyrene pellet and the flame retardant. Claim 17 describes dissolving molecules of the flame retardant that is contained within the polypropylene pellet. Neither the specification nor any claim ever describes "completely extracting" the additives from the sample. Thus, the premise of the written description rejection is incorrect and has, naturally, led to an incorrect conclusion.

Applicants do not quarrel with the Examiner's characterization of the publications mentioned at page 2 of the Office Action which, according to the Examiner's comment, are directed to the complete extraction of additives from polymers. However, those publications, to the extent they stand for that proposition, are irrelevant to the subject matter of the claims that are rejected because those claims

do not require and have never required nor suggested complete extraction of an additive from a polymer pellet.

Applicants have never made a representation in their publications concerning their invention that the novel process requires removal of all molecules of an additive of a plastic sample in order to determine the material dispersed in the pellet and the concentration of that dispersed material. Four of those publications are attached for the Examiner's consideration, although only two of the attached publications are in the English language.

1. Naka et al., *Development of Rapid Screening Method for Brominated Flame Retardants in Plastics by Time of Flight Secondary Ion Mass Spectrometry*, Proceedings of the ISWA World Environment Congress, Rome, Italy, (October 17-21, 2004).

2. Naka et al., *Development of Rapid Screening Method for Brominated Flame Retardants and Hexavalent Chromium by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)*, vol. 48, No. 6, *Shinku*, pp. 365-371 (2005), published by The Vacuum Society of Japan.

3. Naka et al., *Rapid Screening Method for Brominated Flame Retardants and Hexavalent Chromium by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)*, Fourth Intl. Symposium on Environmentally Conscious Design and Inverse Manufacturing, Tokyo, Japan, pp. 818-822, (December 12-14, 2005).

4. Kurokawa, title in Japanese, *Clean Technology*, pp. 29-32 (2005) with partial English language translation.

Since the written description rejection is based upon language that is not part of the claims, i.e., not the claimed invention, that rejection should be withdrawn. If the Examiner believes that the rejection is correct, then Applicants respectfully request reformulation of the rejection, with a citation of the particular language of the claims that is asserted not to be supported by the written description of the patent application

as filed. Then, if that cited portion of the claims is not supported by the patent application as filed, Applicants respectfully request the Examiner supply the factual reasons required in part (B) of MPEP 2163.04 so that a proper written description rejection is stated as required by the cited MPEP section. Then, a more specific response can be prepared.

Further Reply to Comments apparently concerning the Written Description Requirement Rejection. The first complete paragraph appearing at page 3 of the Office Action is not completely understandable. Applicants have not been able to determine the meaning of the portion of the first sentence in which it is alleged that the “specification discloses only examples of preliminary added a specific antioxidant in a known quantity to high-density polyethylene... .” As best understood, this paragraph which may or may not pertain to the written description requirement rejection, suggests that it is unclear how the quantity of additive in a pellet could have been determined.

First, with respect to claim 9, the broadest pending independent claim, the word “analyzing” been changed to “identifying.” Thus, the comment from page 3 of the Office Action, if it is the basis of the written description rejection, is moot with respect to that claim.

The newly added claims, claims 15-18 include two independent claims and, in those claims, the term “analyzing” is used. As already explained, Example 6, appearing at pages 22 and 23 of the patent application as filed (not the substitute specification) supports that claim 15. In the Example 6, a mass spectrum of the residue left by dissolving polystyrene containing a brominated flame retardant was obtained, as shown in Figure 16 of the patent application. Based upon the line in the mass spectrum for silver, since the substrate employed had at least a silver surface, it was possible to produce a quantitative analysis which matched the expected concentration. Of course the concentration of the flame retardant in the pellet was known since the sample was a prepared sample with a known concentration of flame retardant rather than an unknown sample. However, that knowledge was used to

confirm the measurements and to set a standard, not to “jimmy” the results. Moreover, the technique employed was confirmed to be accurate by additional studies made by the inventors. The results of these additional studies appear in the attached writings and publications by the inventors regarding the invention. See the attached publication 1 at its seventh and eighth pages and Figure 8. As explained on that eighth page, confirming tests were made by using CG/MS. Figure 9 of that publication 1 is a graph showing the linear correlation between the analytical results obtained according to the invention and the results obtained using the alternative GC/MS technique. This result confirms what is described earlier in publication 1 and that what is described in the patent application as a proper and reliable quantitative analysis technique. See the same disclosure at pages 369 and 370 of attached publication 2, at pages 820 and 821 of attached publication 3, and pages 30 and 31 of attached publication 4, a partial translation of which is attached.

A similar analytical method with respect to claim 16 is described at pages 26 and 27 of the patent application as filed. With respect to claims 17 and 18, see the description in the patent application with regard to Example 5 at pages 20 and 21 and Example 8 at pages 25 and 26 of the patent application as filed, respectively. The same quantitative analytical techniques are employed in all of those examples which are self-consistent and substantiated by the cited passages of the attached publications, as discussed in the foregoing paragraphs.

The discussion that begins at page 2 in paragraph 5 of the Office Action of December 29, 2010 again directs attention to the written description requirement. Nevertheless, the comment seems to encompass the several different requirements of 35 USC 112, paragraph 1. Thus, the comments in the Office Action are responded to based upon their content, rather than strictly adhering to the particular requirements of that statutory paragraph.

There are several premises of the comments at page 2 of the Office Action which are no longer correct in view of the amendment of the claims. No claim includes the phrase “ a method of analyzing a minute content of a polymer”. The



newly added claims are directed to a method of determining the concentration of the additive or material within the polymer. Claim 9 is directed to a method of identifying the material that is present in a minute amount within a polymer. The Examiner's comments at that part of the Office Action, criticizing the disclosure of the patent application as not matching the claims is now moot. Therefore, to the extent the comments are a ground of rejection that the claim language does not match the disclosure, that ground of rejection is no longer available.

While apparently still discussing the rejection for lack of written description, the Examiner again asserted that the specification does not enable "the second step" which is not particularly identified. Presumably, from the sentence that bridges pages 3 and 4 of the Office Action, the "second step" relates to the "full extraction of the additive from the polymer pellet by contacting only one surface of the pellet with the solvent instead of immersing [sic] the pellet into the solvent." As already discussed above, no claim pending in this patent application, now or earlier, and no part of the specification describes extraction of all of an additive from a polymer pellet. The important feature of the invention is rapid analysis of the content of a polymer pellet, particularly in determining the concentration of a brominated flame retardant *without* extracting all of the flame retardant or other additive from the pellet. Applicants agree that entirely removing an additive is a lengthy process and again point out that one of the important advances provided by the invention is that the analysis can be completed in a period of minutes rather than hours or days. The analysis technique claimed is fully supported by detailed Examples in the patent application, providing a written description of the invention, as claimed. Again, Applicants respectfully request the Examiner to conform the interpretation of the invention to the language of the claims and the disclosure of the patent application. When that revision is made, then the rejection for lack of written description should be withdrawn.

In the event the Examiner still believes that the written description requirement has not been met, then Applicants respectfully request an explanation of the Examiner's position based upon what is claimed, not based upon an interpretation that

goes well beyond the scope of the claimed subject matter. A clear statement of any such renewed rejection with regard to any rejected claims will permit an informed decision with respect to further prosecution of this patent application.

Response to the Lack of Enablement Rejection. The discussion of the rejection pursuant to the portion of 35 USC 112, first paragraph, relating to the enablement requirement appears to begin in paragraph 6 of the Office Action at page 4. In asserting that the subject matter claimed was not enabled for practice by one of ordinary skill in the relevant arts, at page 5 of the Office Action, under the second heading, the Examiner again relied upon the same prior art publications cited with respect to the written description rejection. The Examiner asserting that the “prior art teaches that *complete* extraction of the additives from polymers within a reasonable time frame is a special problem in the art... .” Applicants do not dispute that assertion. However, as stated numerous times above, this comment reflects a misinterpretation or a misunderstanding of what is disclosed and claimed in the patent application.

While repetitive, Applicants again point out that their invention is directed to rapid determination of the presence of and, with respect to some claims, the concentration of, particular additives within polymers in an extremely rapid fashion. The technique is a departure from the prior art publications relied upon by the Examiner. Those publications do pertain to the *complete* extraction of additives from polymers. In the invention, the extraction is decidedly *incomplete*, meaning that only some of the additive is obtained by dissolution. That sample of the additive that is obtained is present in the residue that is left on the substrate that supports the pellet and the solvent that produces the partial extraction. That residue is analyzed to determine the additive and, in some cases, its concentration.

According to MPEP 2164.04, in order to make a proper enablement rejection, the Examiner must first construe the claims. The Examiner construed the word “extract” with respect to the claims initially presented for examination. Assuming, for the sake of argument, that the interpretation made with respect to those claims was

correct, Applicants respectfully point out that all of those originally examined claims were cancelled in response to the first Office Action. The word “extract” does not appear in any claim submitted in response to the first Office Action nor in any claim now pending. Therefore, to the extent the position taken by the Examiner was based upon her interpretation of the word “extracted,” that position can no longer be maintained. Further, the claims that are pending now describe dissolving molecules of the additive material, further demonstrating that there is no attempt to claim a process in which every molecule of an additive within a polymer is extracted in carrying out the claimed process. On this basis, stated in a different way in the preceding paragraphs, Applicants again respectfully request the Examiner to withdraw the enablement rejection. Again, if the enablement rejection is reasserted, then Applicants respectfully request a restatement of any maintained rejection, citing the specific claim language that provides the predicate of the rejection.

The enablement requirement has been met here because the specification contains a teaching of the manner and process of making and using the *claimed* invention, according to the claims now pending. According to MPEP 2164.04, that disclosure must be taken as in compliance with the enablement requirement because there is no reason to doubt the objective truth of the statements contained in the disclosure. That same section of the MPEP points out that

“it is incumbent upon the Patent Office, whenever a rejection on this basis is made, to explain *why* it doubts the truth or accuracy of any statement in a supporting disclosure and to back up assertions of its own with acceptable evidence or reasoning which is inconsistent with the contested statement. Otherwise, there would be no need for the applicant to go to the trouble and expense of supporting his presumptively accurate disclosure.” Citing *In re Marzocchi*, 169 USPQ 367, 370 (CCPA 1971). [Emphasis in original.]

Again, Applicants emphasize that the Examiner’s position and reliance upon the prior art publications cited at page 5 of the Office Action is reasonable if the

claimed subject matter required or encompassed complete extraction of an additive from a polymer. However, no such disclosure appears in the patent application or in the claims now pending. Further, the claims now pending are not susceptible to the apparent claim interpretation made by the Examiner with respect to the originally examined claims, all of which have been cancelled.

In commenting on the examples provided in the patent application, at page 6 of the Office Action, the Examiner stated that there is no confirmation in the patent application of the alleged linear correlation between the analytical data and the relative concentration of the additives. Respectfully, Applicants understand this statement to be an assertion that they have been untruthful in describing their invention. The Examiner's assertion, which is fundamental to the propriety of the non-enablement rejection, is contrary to the statement in *Marzocchi* that a disclosure is presumptively accurate. Further, while the patent application may not contain such confirmation, that confirmation was made and is part of each of the four publications listed above and supplied with this Reply. As discussed above, similar or identical graphs in each of those publications confirm, by comparing results obtained according to the invention with tests made pursuant to an acceptable international standard test employing GC/MS. These results prove that the Examiner's suspicions, if permitted pursuant to well-established U.S. patent law, are incorrect. For that further reason, the foundation of the non-enablement rejection is unsound and the rejection should be, upon reconsideration, withdrawn.

At pages 6 and 7 of the Office Action, the Examiner acknowledged that the patent application is enabling with respect to measuring content of brominated flame retardant in a polymer, but asserted that claim 10 was too broad in view of the disclosure of the patent application. Applicants disagree for the reasons presented above in traversing, generally, the non-enablement rejection. Further, Applicants point out that new claim 16, which includes a limitation somewhat similar to examined claim 10, is clearly enabled based upon the Examiner's remarks.

Finally, the Examiner pointed out that one measure of whether the enablement requirement has been met is the number and quality of the working examples included in a patent application. Here, there are nine highly specific working examples. These examples further corroborate Applicants' position that the disclosure is enabling in view of the scope of the currently pending claims.

For the foregoing reasons, Applicants submit that the rejections pursuant to both of the distinct requirements of 35 USC 112, first paragraph, are incorrect with regard to the subject matter as presently claimed and disclosed in the patent application. Therefore, upon reconsideration, those rejections should be withdrawn.

*Rejections Pursuant to 35 USC 112, Second Paragraph and Response*

As understood, the rejection of claims pursuant to the second paragraph of 35 USC 112 is based upon particular language of claims 9 and 10. The rejection is respectfully traversed.

The language cited from claim 9 as indefinite either no longer appears in that claim or has been clarified. The first paragraph of claim 9 has been amended in a way that makes apparent that the additive material referred to in that paragraph is the same additive material referred to in the preamble of the claim. In addition, a person of skill in the art would understand that those additive materials, present in a minute amount in the polymer material, are the same in the preamble and the first paragraph of claim 9. It is apparent that the additive material that is present in the minute quantity in the polymer pellet must be different in composition from the polymer material, otherwise there would be nothing to identify within the polymer material. However, that requirement is now expressly stated.

The comment with respect to the third paragraph of claim 9 again includes the misinterpretation that the claim and the disclosure describe complete extraction of the additive material from the polymer material. This misinterpretation is extensively responded to above. In a further attempt to avoid continuation of that misinterpretation, the word "extracting" no longer appears in claim 9 in any form so

that there is not even attenuated support for the incorrect interpretation of the claims that has been previously made. Further, Applicants submit that dependent claim 10 is sufficiently definite and, therefore, does not require amendment. The word “analyzing” does not appear in the preamble, only in the final paragraph, of claim 9. In view of the amendments of claims 9-14 and the foregoing remarks, the rejection pursuant to 35 USC 112, second paragraph, should be withdrawn.

*Prior Art Rejections and Response*

Claims 9, 11, and 13 were rejected as unpatentable over Oguro (JP 2001-77158) in view of a non-patent publication to Medard. There was no prior art rejection of claims 10, 12, and 14. This rejection is respectfully traversed.

Applicants again respectfully note that throughout the characterization of the disclosure of Oguro, reference is made to “aqua region 3.” Some clarification may appear at page 11 of the Office Action. Aqua regia is a mixture of sulfuric and nitric acids, a mixture that dissolves gold. In view of the Examiner’s lengthy service at the U.S. Patent and Trademark Office and high level of knowledge in the chemical arts, it is disappointing that this apparent translation error appearing in the English language abstract of Oguro was carried forward in the Office Action of December 29, 2010.

Agua regia is, of course, not an organic solvent as is the solvent referred to in all of the claims that were previously examined and are still pending, and in all of the newly added claims. Oguro is directed to identifying metallic contamination on the surface of a silicon wafer. Of course, a silicon wafer is not a polymer material. There simply is no relationship between Oguro and the invention as claimed in claims 9-18.

The foregoing comments, made in a somewhat different form in response to the first Office Action, appear to have been dismissed by the Examiner because the previous prior art rejection was for obviousness, not for anticipation. Further, the Examiner seems to have stated at page 11 of the Office Action of December 29, 2010 that she maintained the rejection, although changing its form, because the argument

previously present against the application of Oguro was not sufficiently strong. Applicants respectfully protest this kind of reply.

When a rejection is based upon a reference that is remote from what is claimed, as is Oguro with respect to claims 9-14, the amount of argumentation required to refute the rejection need not be extensive. Applicants request the Examiner give appropriate weight to the quality of the arguments presented, rather than their quantity. Merely citing a prior art publication describing the washing of a surface of a material, as in Oguro, does not present a reasonable ground for a prior art rejection of any of claims 9-18.

It was not explained previously how one of skill in the art would make a leap of faith from the extraordinarily corrosive aqua regia solution of Oguro for stripping metallic contaminants from the *surface* of a silicon wafer to using a non-corrosive organic solvent to dissolve an additive material dispersed within a polymer. There is not the slightest commonality between the solvent materials or the materials being treated in Oguro and the invention.

In explaining the rejection, as best understood from page 11 of the Office Action, the Examiner asserted that she had established obviousness “since the method [of Oguro] applied to dissolving contaminants *in* the silicon wafer is exactly the same as the method recited in the instant claims for the polymer and additives.” (Emphasis added.) Applicants respectfully disagree with several parts of this remark, which apparently reflects yet another misunderstanding.

In Oguro, it is only *surface* metallic contamination that is or can be removed from the crystalline silicon wafer. It is impossible for the aqua regia to penetrate and remove from within the silicon wafer any internal metallic contamination. The Examiner’s attention is directed to paragraphs [0002]-[0007], [0009], [0012], [0013], [0016], [0017], [0021], [0024]-[0026], and [0032] of the computer-generated English language translation of Oguro that is readily available from the JPO website and a copy of which is attached. Those paragraphs *expressly* state that Oguro is directed to the removal of contamination from the surface of the silicon wafer. Oguro never even

suggests that his process can liberate any contamination from within a silicon wafer. No one of ordinary skill in the semiconductor arts would ever interpret the disclosure of Oguro any other way or contemplate that Oguro describes the extraction of any metallic contamination from within a silicon wafer. To the extent the Examiner has construed Oguro as describing dissolving some additive from within a silicon wafer, that interpretation is incorrect, unsupported by Oguro, and is contrary to well-established knowledge in the art. No proper rejection can be founded upon such an unscientific and unsupportable interpretation of Oguro.

Since Oguro does not relate to extracting an internally dispersed additive from a material, even disregarding the differences between an extraordinarily corrosive acid mixture and an organic solvent, and between silicon, an inorganic material, and a polymer material, nothing in Oguro would suggest to a person of ordinary skill in the art, as seems to have been asserted in both Office Actions, the dissolution of a minority additive dispersed within a host polymer.

As apparently cut and pasted from the previously Office Action, Oguro was characterized as analyzing some residue of the aqua regia, a residue which was subsequently dissolved in nitric acid, by “inductively coupled plasma mass spectrometry or atom absorption spectrometry” No attempt was previously made correlate those analytical techniques with time-of-flight secondary ion mass spectrometry, the technique expressly employed in claims 9-14 (and new claims 15-18). Now, Medard is apparently relied upon as describing the ToF/SIMS analytical technique.

Applicants agree that Medard describes ToF/SIMS. That technique is well known in the semiconductor arts for analyzing, essentially atomic layer by atomic layer, the composition of semiconductor structures. In this technique, a sample is bombarded by relatively heavy ions which dislodge, i.e., sputter, ions from the surface of the sample being bombarded. The dislodged ions are directed to a mass spectrometer where the masses of those ions are determined. The ion masses reveal the chemical elements of the ions. By observing the masses over a period of time, the



composition, layer-by-layer, of the sample can be determined. In Medard, the sample is a polymer that contains an additive and the sputtering process (ToF-SIMS) enables determination of the distribution of the additive within the sample, with respect to what is, initially, an exterior surface of the sample.

In the invention, it is the residue, left by the treatment of the sample with the solvent, that is present on a substrate, preferably having a silver surface, that is subjected to ToF/SIMS in order to determine the composition of the additive. As best understood, the theory of the prior art rejection is that modifying Oguro by employing ToF/SIMS would produce the invention claimed. Clearly, that conclusion is not supported by Oguro and Medard with respect to examined claims 9-14 and has no possibility of being correct with respect to claims 15-18.

Even if it is assumed that it would have been obvious to have replaced the spectrometry techniques described by Oguro with ToF/SIMS, there is still no description or teaching in either Oguro or Medard for obtaining a sample of an internally dispersed additive from a polymer, using a solvent, leaving a residue from the dissolution process on a substrate, and analyzing the residue by ToF/SIMS. Medard describes applying ToF/SIMS to a polymer sample, but does not describe treating the polymer sample with a solvent in order to obtain, and thereby identify and analyze, the additive of the polymer. As already explained, Oguro describes using a highly corrosive mixture to dissolve metallic contamination from the surface of a silicon wafer, not from within the silicon wafer. Therefore, together, Oguro and Medard lack any teaching concerning obtaining an additive from within a polymer, using a solvent, and subsequently analyzing the residue left from that process on the substrate on which the dissolution process has taken place. Absent that critical part of all pending claims, it is impossible for Oguro, even as modified by Medard, to suggest the invention claimed in claims 9-18.

With respect to newly added claims 15-18, it is plainly apparent that no potential modification of Oguro with Medard could include all of the highly specific

limitations of those claims. Accordingly, upon reconsideration, the prior art rejection should be withdrawn.

### *Final Comments*

In preparation of this Reply, detailed attention was given to every part of the Office Action dated December 29, 2010. A few of its remarks are not responded to above so that a reply is now given. For example, at page 10 of the Office Action, reference was made to the shape of the pellet of polymer material. "Also, why the pellet has only one surface? There is no such thing as a two-dimensional pellet." This question and comment are not understood because no claim makes any reference to any shape of any pellet or even of any surface of any pellet. Of course, drawings of the patent application show a pellet as a parallelepiped. That schematic representation is only provided to assist in understanding the disclosure of the patent application and the so-called single drop micro-extraction technique. Just as Applicants are prohibited from importing into the claims disclosure of a patent application, so it would be wrong for the Examiner to incorporate into the claims particular pellet configurations based upon the drawings of the patent application. Thus, since no claim describes a pellet of a particular shape, further response to the question and remark is not necessary nor provided.

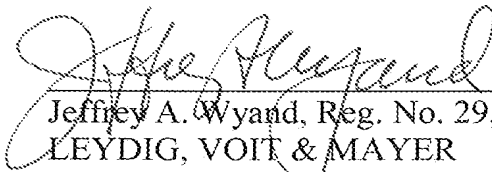
With regard to the assertion that the additive is already known in the samples analyzed in the examples of the patent application, it is not understood how that fact, in demonstrating the operability of the invention, has any relevance to its patentability. Further, as explained before, a particularly useful application of the invention is in the detection of prohibited brominated flame retardants in plastics. Those plastics may be present in electronic products shipped into the European Union. In other words, an important application of the invention is seeking to identify the presence of, and the concentration of, a particular additive in a polymer. That application of the invention in attempting to identify a particular additive does not and should not affect the patentability of the claims. Instead, the benefit conferred by the invention should be

considered, along with the differences between the invention and the prior art, in determining patentability. Creation of standardized samples as references or standards for use in the novel process and in verifying that the process is successful based on those standards, does not create a circularity that adversely affects patentability of the claimed invention.

*Conclusion*

Since, for the reasons presented here, the claims now pending, claims 9-18, are patentable, upon reconsideration, the rejections should be withdrawn, and claims 9-18 should be allowed.

Respectfully submitted,

  
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# DEVELOPMENT OF RAPID SCREENING METHOD FOR BROMINATED FLAME RETARDANTS IN PLASTICS BY TIME OF FLIGHT SECONDARY ION MASS SPECTROMETRY

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## ABSTRACT

By Directive on RoHS, the use of six hazardous substances is restricted to new electrical and electronic equipment put on the market in Europe from 1 July 2006. The estimation of the type and the content of brominated flame retardants is necessary in plastics of the equipment and the parts. The new technique by using time-of-flight secondary ion mass spectrometry (TOF-SIMS) is proposed for rapid screening test of these substances. We named this technique one drop extraction method.

The sampling method of brominated flame retardants in plastic materials with toluene on silver substrate was investigated for analysis of trace organic compounds by TOF-SIMS. High impact polystyrene(PS) and polypropylene (PP) plates were prepared as evaluation samples containing Decabromodiphenylether(DeBDE) of 0.01-10wt%. Evaluation time that includes sample pretreatment time and measurement time was about 1 hour. The positive quasi-molecular ion  $(\text{DeBDE}+\text{Ag})^+$  (DeBDE cationized with Ag) was suitable for estimation of DeBDE. It was proved that content and spectral intensity had the clear magnitude correlation within 0.01-10wt% content of DeBDE.

It was found that the quick decision of whether the brominated flame retardants in the plastics is the substance restricted or not by Directive on RoHS is possible by this method. We can screen the substances in wide range of content of 0.01-10wt%. As a result, it can be expected that hazardous substance management which concerns Directive on RoHS/WEEE becomes more reliable.

## INTRODUCTION

By Directive on RoHS<sup>[1]</sup> (restriction of the use of certain hazardous substances in electrical and electronic equipment), the use of six hazardous substances (lead, cadmium, hexavalent chromium, mercury, and two brominated flame retardants (polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE))) is restricted to new electrical and electronic equipment put on the market in Europe from 1 July 2006. The regulation value of cadmium is 0.01wt%, and others are 0.1wt% in materials. PBDE receives restriction according to the number of bromine. [The European Commission is evaluating the application for

Decabromodiphenylether(DeBDE).] Therefore we should exclude hazardous substances from electrical and electronic equipments and control strictly. It is necessary to estimate materials and parts in electrical and electronic equipments and to collect information of content of hazardous substances.

However, because it is impractical that all of a large number of materials and parts in electrical and electronic equipments are estimated precisely, we require a screening method for estimating approximate content of hazardous substances in a short time. Recently energy dispersion X-ray fluorescence spectrometry (XRF) has become useful for element screening, which can estimate the content of the elements in metals, ceramics and resins at ppm level. Although we can estimate concentration of total chromium in materials by this method, it is difficult to distinguish hexavalent chromium from trivalent chromium. Although we can estimate concentration of total bromine by this method, it is impossible to identify the kind of brominated flame retardants. Estimation of the type and the content of brominated flame retardants is necessary in plastics of the equipment and the parts, and control of the content of additive agents is important in recycled plastic materials for development of plastic recycle technology. Although application of gas chromatography mass spectrometry (GC/MS) is useful for the precise determination of trace brominated flame retardants in water, soil, sediment, and tissue<sup>[2]</sup>, this method generally needs a long time for sample preparation and measurement.

In contrast, TOF-SIMS is suitable for obtaining structural and quantitative information of trace organic compounds in a relatively short time. Recently high sensitive detection methods by TOF-SIMS have been reported for various polymers on a silver substrate<sup>[3][4][5][6][7][8][9]</sup>. In these papers, quasi-molecular ion cationized with  $\text{Ag}^+$  have been used for the polymer analysis. We applied this method to the detection of brominated flame retardants of which molecular weight ranges from several hundreds to several thousands.

In this paper, we examined the ability of TOF-SIMS to estimate approximate content of brominated flame retardants in plastic materials. It was found that a sample preparation of extraction of those on silver substrate is effective to TOF-SIMS measurement and this method is useful for judgment of suitability of plastics for Directive on RoHS. We named this method one drop extraction method.

## EXPERIMENTALS

### TOF-SIMS Measurement

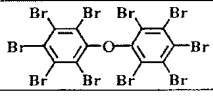
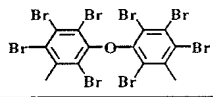
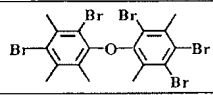
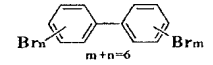
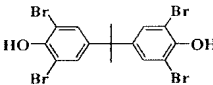
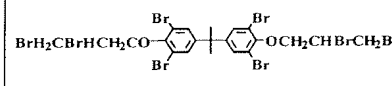
Spectra of time of flight secondary ion mass spectrometry were obtained by using TOF-SIMS instrument (Model2100 TRIFTII, Physical Electronics(PHI), Inc.). The instrument has the advantage of high transmission efficiency over wide mass range (e.g., 1-1200). The mass resolution ( $\Delta M/M$ ) is approximately 5000 at half peak height. A sample area of  $50\mu\text{m} \times 50\mu\text{m}$  is bombarded by 15 KeV  $^{69}\text{Ga}^+$  with an average current of 2nA. In quantitative analysis, average of peak intensities of 3 measurement points in a substrate was used. Peaks in TOF-SIMS spectra can be distinguished by their  $m/z$  values and peak intensity patterns.

### Regents and Sample Preparation

As standard regents of brominated flame retardants, the following six kinds of regents were used; Decabromodiphenylether[DeBDE]( $>98\%$ , Wako Pure Chemical Industries, Ltd., Japan), Octabromodiphenylether[OcBDE] ( $50\mu\text{g/ml}$  2,2',3,3',4,4',6,6',-Octabromodiphenylether in toluene)(WELLINGTON LABORATORIES, Inc., Ontario, Canada), Pentabromodiphenylether [PeBDE]( $50\mu\text{g/ml}$  2,2',4,4',5-Pentabromodiphenylether in isooctane) (AccuStandard, Inc., CT, USA), polybrominated biphenys [PBB] ( $100\mu\text{g/ml}$  FiremasterBP-6 in isooctane) (AccuStandard, Inc., CT, USA), tetrabromobisphenol-A [TBA] (FG-2000, TEIJIN

CEMICALS LTD., Japan), tetrabromobisphenol-A-bis[2,3-dibromopropylether] [TBA-BP] (FG-3100, TEIJIN CEMICALS LTD., Japan). Table 1 shows chemical structures and molecular weights of those.

Table 1. Characteristics of brominated flame retardants

Compound	Composition	Molecular Weight	Structure
Decabromodiphenylether (DeBDE)	C <sub>12</sub> OBr <sub>10</sub>	959.17	
2,2',3,3',4,4',6,6'-Octabromodiphenylether (OcBDE)	C <sub>12</sub> H <sub>2</sub> OBr <sub>8</sub>	801.38	
2,2',4,4',5-Pentabromodiphenylether (PeBDE)	C <sub>12</sub> H <sub>5</sub> OBr <sub>5</sub>	564.70	
Polybromobiphenyl (firemaster BP-6) (PBB)	C <sub>12</sub> H <sub>m</sub> -1Br <sub>m</sub> (m=1~10)	627.60 (m=6) 706.49 (m=7) 785.38 (m=8)	
Tetrabromobisphenol-A (TBA)	C <sub>15</sub> H <sub>8</sub> O <sub>2</sub> Br <sub>4</sub>	543.90	
Tetrabromobisphenol-A-bis[2,3-dibromopropylether] (TBA-BP)	C <sub>21</sub> H <sub>20</sub> O <sub>2</sub> Br <sub>8</sub>	943.66	

Standard resin samples containing 0.01, 0.1, 1 and 10wt% of DeBDE were prepared using a laboratory mixer with a heater for testing of extraction of brominated flame retardant from plastic materials.

As a substrate for ToF-SIMS measurement, silver foil (99.99%, 0.125mm thick, Sigma-Aldrich, Co., MO, USA) was used. The silver substrate was cut into 15mm\*15mm strips, and cleaned with toluene and acetone using a washer with ultrasonic wave.

#### Measurements for standard reagents

1mg/ml test solutions of DeBDE, TBA and TBA-BP were prepared by dissolving those reagents in toluene. Those of OcBDE, PeBDE and PBB were prepared by concentration of 50 µg/ml or 100 µg/ml standard solutions.

TOF-SIMS spectra of the standard reagents were obtained from deposition of a 10µL test solution by a micropipette on a silver substrate.

#### Measurements for extract of brominated flame retardants from plastic materials on substrate

Extraction of brominated flame retardants from plastic materials on a silver substrate was done by the following procedures. First, a test piece of 3mm\*3mm was put on center of silver substrate, and 10µL of toluene as solvent for extraction of brominated flame retardants was dropped on the test piece. Then, the substrate was put in a sealed glass chamber containing 1ml

of toluene for 10 minutes in order to prevent vaporization of the solvent. The test piece was taken away by a pinset and the residue was air-dried.

TOF-SIMS spectra of extract of brominated flame retardants from plastic materials were obtained from the surface of the substrate. The total time of procedures and measurement was about 35-60 minutes per one sample.

## RESULTS AND DISCUSSION

### Spectra of standard reagents

Figure 1 shows a positive TOF-SIMS spectrum of DeBDE (MW=959.17) in the mass region  $m/z=0-1200$ . The intense peak in the mass region  $m/z=1050-1080$  corresponds to quasi-molecular ion cationized with  $\text{Ag}^+$ ,  $(\text{DeBDE}+\text{Ag})^+$  (MW=1067.04), and the weak peak in the mass region  $m/z=900-920$  corresponds to  $((\text{DeBDE}-2\text{Br})+\text{Ag})^+$  (MW=907.23). It seems that  $((\text{DeBDE}-2\text{Br})+\text{Ag})^+$  was generated by abstraction reaction of two bromines from DeBDE and cationization with  $\text{Ag}^+$ . Peaks due to molecular ions cationized without  $\text{Ag}^+$ , shown as  $\text{DeBDE}^+$  (MW=959.17) and  $(\text{DeBDE}-2\text{Br})^+$  (MW=799.36) in figure 1, are also observed. Peak intensity of  $(\text{DeBDE}+\text{Ag})^+$  is about 10 times higher than that of  $\text{DeBDE}^+$  ion.

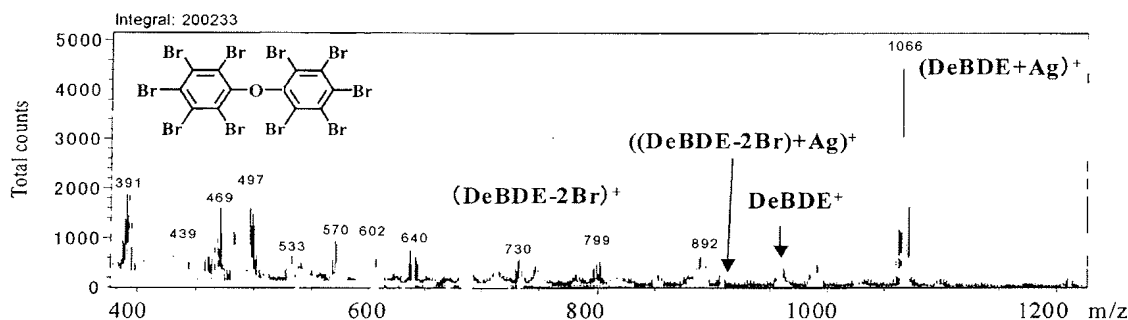


Figure 1. Positive TOF-SIMS spectrum of DeBDE as standard reagent

Figure 2 shows a negative TOF-SIMS spectrum of DeBDE in the mass region  $m/z=0-1200$ . The intense peaks in the mass region  $m/z=1-300$  are due to  $\text{Br}^-$ ,  $\text{Br}_2^-$  and  $\text{Br}_3^-$ . In addition, there are four weak peaks;  $\text{C}_6\text{Br}_5\text{O}^-$ ,  $(\text{DeBDE}+\text{Ag})^-$ ,  $((\text{DeBDE}-2\text{Br})+\text{Ag})^-$  and  $\text{DeBDE}^-$ .

It appears that quasi-molecular ion  $(\text{DeBDE}+\text{Ag})^+$  shown in figure 1 is suitable for identification and quantification of DeBDE, because peak intensity of this ion is the most intense and peak pattern of this ion reflects the molecular structure.

Figure 3 shows positive TOF-SIMS spectra of OcBDE (MW=801.38), PeBDE (MW=564.70) and PBB in the mass region  $m/z=400-1200$ . The use of those compounds will also be restricted in electrical and electronic equipment. Intense peak due to quasi-molecular ion of  $(\text{OcBDE}+\text{Ag})^+$  (MW=909.25) and  $(\text{PeBDE}+\text{Ag})^+$  (MW=672.57) was observed respectively in the spectrum of OcBDE and that of PeBDE in a similar way to DeBDE in the positive spectrum. In the spectrum of firemasterBP-6 as PBB reagent, peaks of  $(\text{HxBB}+\text{Ag})^+$  (MW=735.46),  $(\text{HpBB}+\text{Ag})^+$  (MW=814.36) and  $(\text{OcBB}+\text{Ag})^+$  (MW=893.25) were observed. PBDE and PBB having the different number of bromine can be distinguished by the  $m/z$  number of quasi-molecular ion  $(\text{M}+\text{Ag})^+$  (M: molecule).

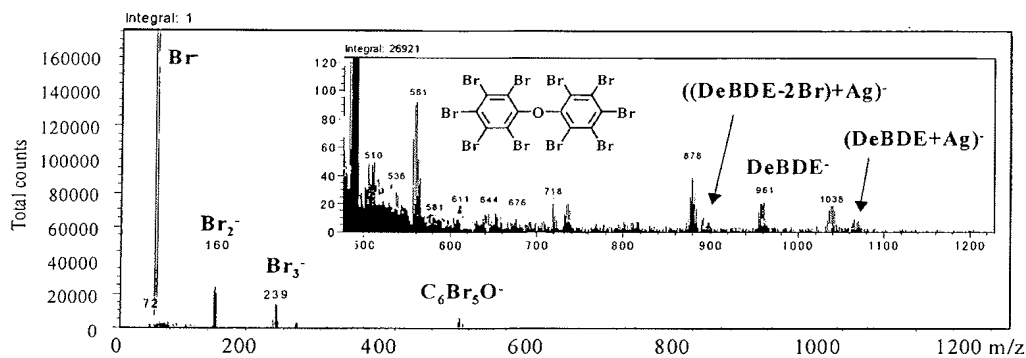


Figure 2. Negative TOF-SIMS spectrum of DeBDE as standard reagent

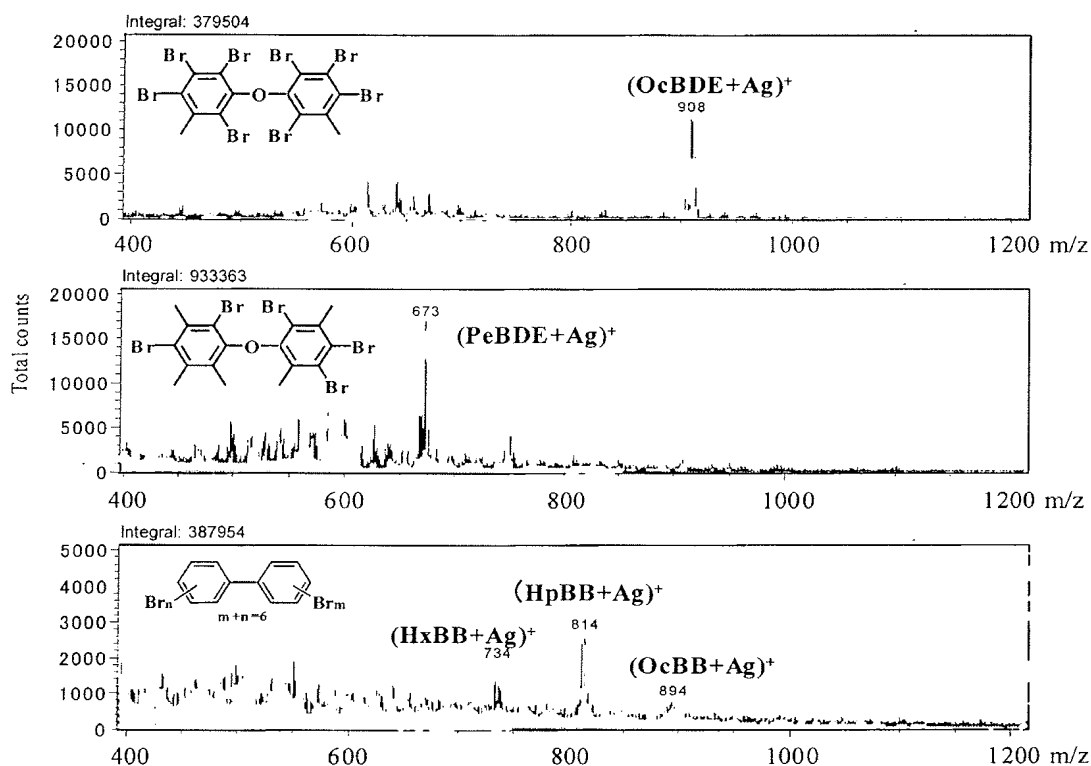


Figure3. Positive TOF-SIMS spectrum of OcbDE, PeBDE and PBB as standard reagent

Figure 4 shows positive spectra of DeBDE and OcbDE in the mass region  $m/z=890-925$ . The calculated isotopic patterns due to bromine atoms are marked with horizontal bars and are in agreement with peak intensity patterns observed in the actual spectra. It was found that isotopic patterns of  $((\text{DeBDE}-2\text{Br})+\text{Ag})^+$  and  $(\text{OcbDE}+\text{Ag})^+$  are observed in the approximately same mass region. However, we can discriminate between two compounds by comparing the  $m/z$  number of the highest peaks of both. From these results, it is clear that all brominated flame retardants restricted by Directive on RoHS could be detected and identified by quasi-molecular ion cationized with  $\text{Ag}^+$  in positive ion measurements by TOF-SIMS.



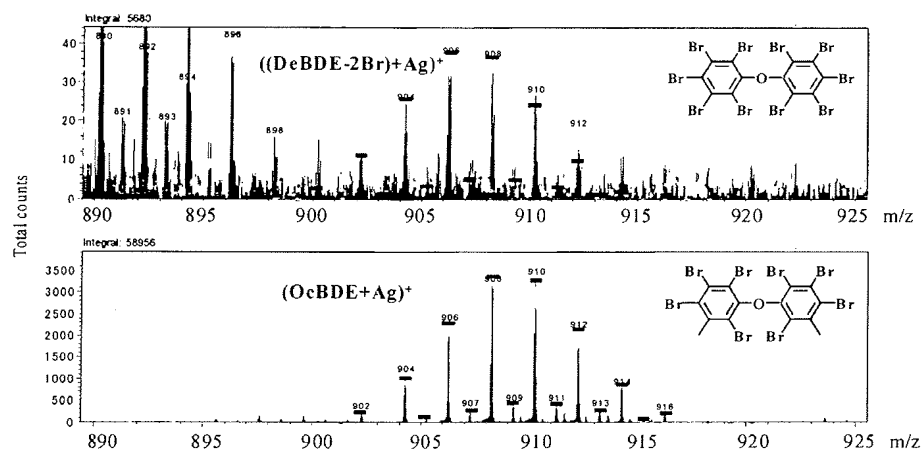


Figure4. Positive TOF-SIMS spectrum of DeBDE and OcBDE as standard reagent in the mass region  $m/z=890-925$

Next we examined TBA and TBA-BP as representatives of unrestricted brominated flame retardants by Directive on RoHS. Figure 5 shows positive TOF-SIMS spectra of TBA (MW=543.90) and TBA-BP (MW=943.66) in the mass region  $m/z=400-1200$  together with spectrum of DeBDE. Quasi-molecular ions with cationized  $\text{Ag}^+$ , shown as  $(\text{TBA}+\text{Ag})^+$  (MW=651.76) and  $(\text{TBA-BP}+\text{Ag})^+$  (MW=1051.52), were obtained and their  $m/z$  numbers differs from those of  $(\text{DeBDE}+\text{Ag})^+$ .

It was found that PBDE and PBB were distinguished from other brominated flame retardants by TOF-SIMS.

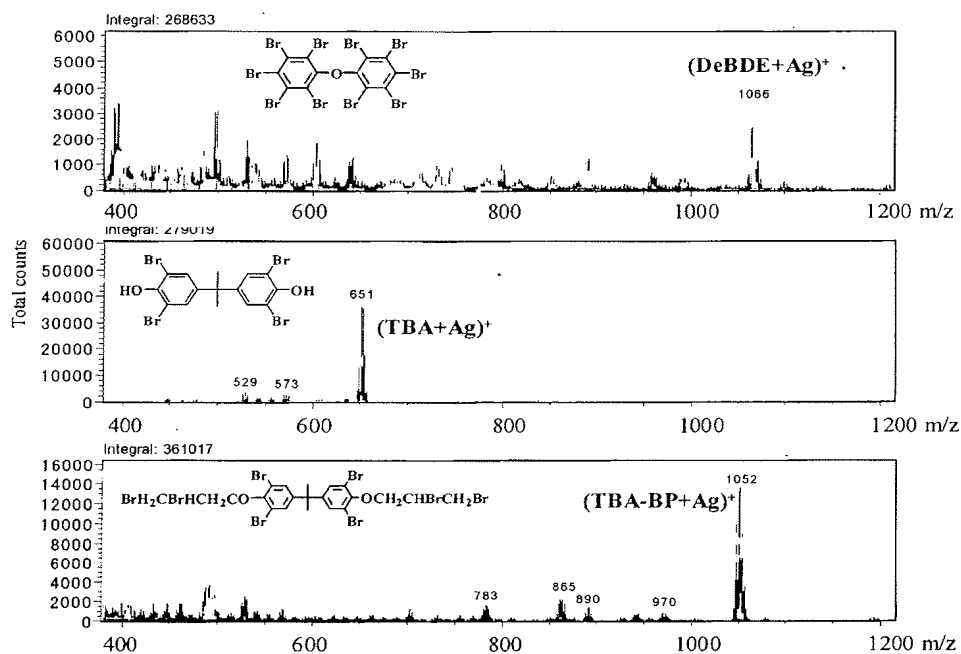


Figure5. Positive TOF-SIMS spectrum of DeBDE, TBA and TBA-BP in the mass region  $m/z=400-1200$

### Examination of quantification of brominated flame retardant in plastic materials by one-drop extraction method

The relation between concentrations of DeBDE in plastic materials and peak intensities of  $(\text{DeBDE}+\text{Ag})^+$  was examined for standard resin samples containing 0.01, 0.1, 1 and 10wt% DeBDE on a silver substrate by one drop extraction method using TOF-SIMS.

Figure 6 shows positive TOF-SIMS spectrum of PS containing 1wt% DeBDE in the mass region  $m/z=400-1200$ . Quasi-molecular ions with cationized  $\text{Ag}^+$ , shown as  $(\text{DeBDE}+\text{Ag})^+$ , was observed in the same way as observed in the positive spectrum of standard reagent. Detection of  $(\text{DeBDE}+\text{Ag})^+$  was not interfered with fragment peaks in the mass region  $m/z=400-800$ , which derived from polystyrene resin and other additives (e.g., antioxidant, etc.). Figure 7 shows positive TOF-SIMS spectrum of PS containing 0.01wt% DeBDE in the mass region  $m/z=1040-1090$ . Clear peaks of  $(\text{DeBDE}+\text{Ag})^+$  were obtained. DeBDE in PP can be identified in the same method.

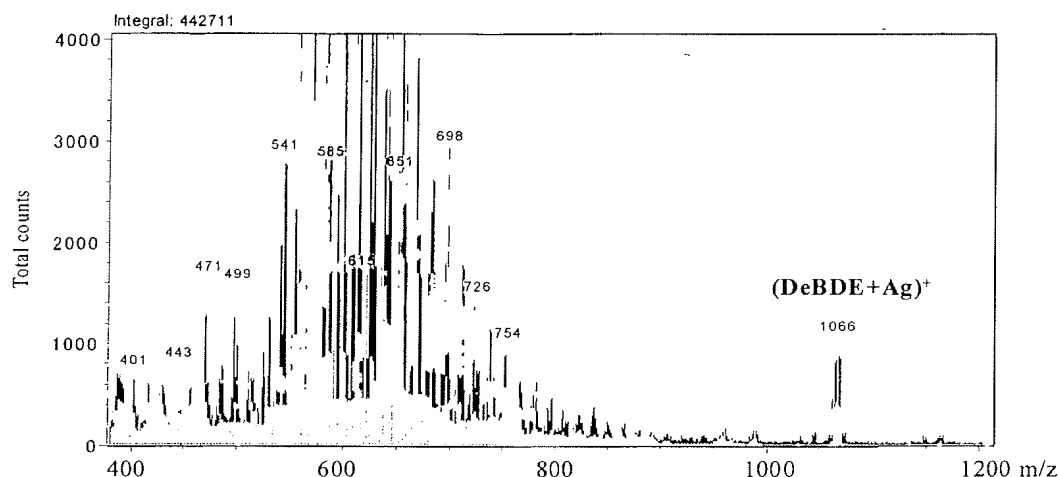


Figure6. Positive TOF-SIMS spectrum of PS containing 1wt% DeBDE

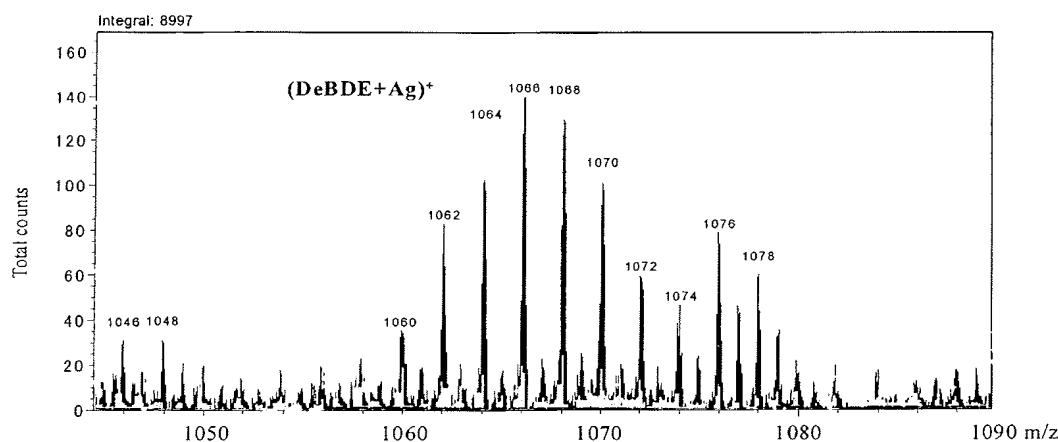


Figure7. Positive TOF-SIMS spectrum of PS containing 0.01wt% DeBDE

We plotted three data points of  $(\text{DeBDE}+\text{Ag})^+$  intensities normalized to  $\text{Ag}_2^+$  at each nominal concentration of DeBDE in figure.8. There is a clear dependence of normalized

intensities to nominal concentrations of  $(\text{DeBDE}+\text{Ag})^+$  in the range from 0.01wt% to 10wt%. Therefore, it was ensured that the concentration of DeBDE in plastic materials could be estimated by one drop extraction method using TOF-SIMS over the range from 0.01wt% to 10wt%.

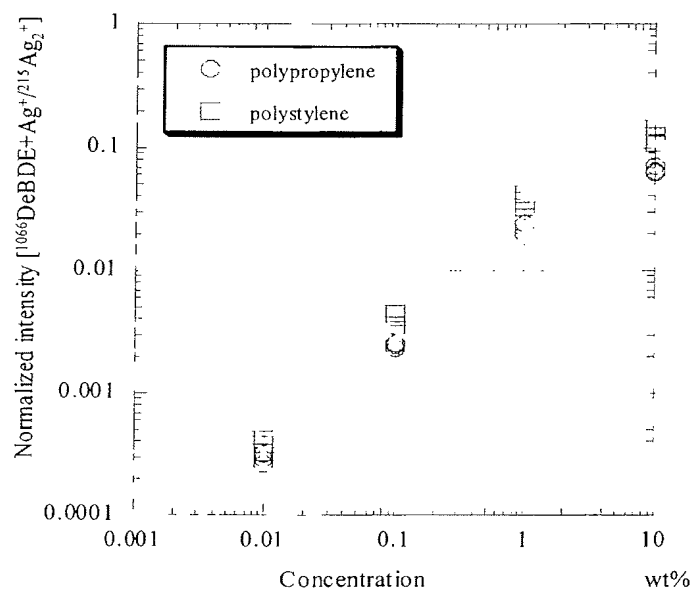


Figure 8. Plots of normalized peak intensity of  $(\text{DeBDE}+\text{Ag})^+$  versus concentration of DeBDE in PS and PP

### Comparison between gas chromatography mass spectrometry (GC/MS) and one drop extraction method using TOF-SIMS

It is well known that GC/MS is the useful analytical method for the precise determination of brominated flame retardants. Each isomer of PBDE and PBB can be measured separately by this method. We compared the concentrations estimated by one drop extraction method with those determined by usual analytical method using GC/MS.

Test resin samples were prepared by the following procedures. Pieces of plastic materials (PS or PP) in the course of plastics separation process at a recycling factory for electrical and electronic equipments, were melted using a laboratory mixer with a heater and plates were made using hot-press equipment.

Test resin samples containing DeBDE as the concentration of 0.041-10wt% determined by GC/MS, were measured by one drop extraction method. Figure 9 shows the relation between the concentrations by one drop extraction method and by GC/MS, where the former concentrations were estimated by utilizing the linear relationship between the normalized intensities by TOF-SIMS and nominal concentrations in figure 8. As shown in figure 9, an excellent correlation ( $r=0.976$ ) was observed between the concentrations by two methods. Therefore, it was found that we can obtain the DeBDE concentration in plastic materials in a short time using one drop extraction method.

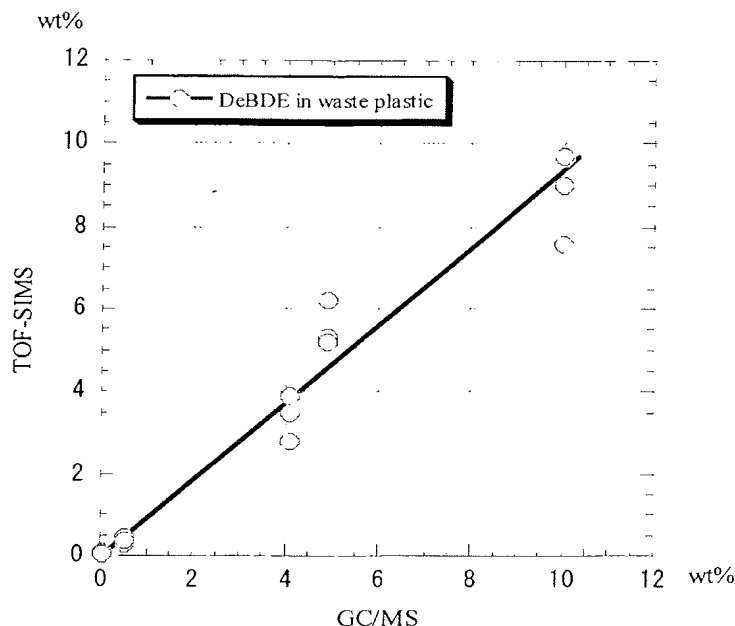


Figure9. Comparison between the concentration estimated by one drop extraction method and determined by GC/MS

## CONCLUSION

It was confirmed that one drop extraction method using TOF-SIMS is a very powerful technique for the rapid screening test of DeBDE in plastic materials. We could identify the kind of brominated flame retardants, could distinguish the unrestricted compounds from the restricted ones by Directive on RoHS and could estimate the concentration of brominated flame retardants in the range of 0.01-10wt% by utilizing TOF-SIMS. It is concluded that we can judge whether the use of the specific plastics are allowed or not in electrical and electronic equipments in a relatively short time.

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## 一滴抽出法による臭素系難燃剤および六価クロムの短時間分析\*

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## Development of Rapid Screening Method for Brominated Flame Retardants and Hexavalent Chromium by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

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## 1. 緒 言

欧州における RoHS (restriction of the use of certain hazardous substances in electrical and electronic equipment) 指令<sup>1)</sup>により2006年7月1日以降 EU 加盟国内に上市する電気電子機器に対して6種類の有害物質(鉛, カドミウム, 六価クロム, 水銀, 臭素系難燃剤2種類(ポリブロモジフェニルエーテル (PBDE), ポリブロモビフェニル (PBB))の使用制限が発効される。各物質の使用制限に係るしきい値は, カドミウム100 ppm, 鉛, 六価クロム, 水銀, PBDE および PBB 1000 ppm となる予定である。PBDE はその臭素数により規制される(臭素数5および8を規制予定, 10は調査中)。これに伴い, 電気電子機器の使用部品や材料に含まれる使用制限物質を全廃し, 厳しく管理する必要がある。使用制限物質の管理には, 含有情報調査に加えて, 含有量不明の部品・材料の分析評価が必要である。

しかし, 電気電子機器に使用される膨大な数の部品・材料全てを対象に精密な分析は実質的に不可能である。そのためおおよその含有量を判定可能な, 簡易で迅速なスクリーニング技術が必要となる。

近年, 材料の元素分析装置としてエネルギー分散型蛍光 X 線分析装置が汎用化され, 金属, セラミックス, 樹脂などに含まれる金属を ppm レベルで評価可能となっており, 測定試料の前処理はほとんど必要なく1分間程度でおおよその含有量を把握できるものである。しかし, 元素分析法のため各元素の含有量は判定可能であるが, 有機物である臭素系難燃剤の同定は不可能であり, 六価クロムと他の価数のクロムとの判別は困難である。

微量の臭素系難燃剤の精密分析方法としては, 環境水や土壌を対象としたガスクロマトグラフ質量分析法<sup>2)</sup>の応用, 六価クロム定量はジフェニルカルバジド吸光光度法<sup>3)</sup>が一般的であるが, いずれも前処理操作が複雑であり分析所要時間が数時間から数日と長い。

微量物質の検出および構造情報が得られる分析法として,

飛行時間型二次イオン質量分析法 (TOF-SIMS: Time of flight-secondary ion mass spectrometry) があり, 臭素系難燃剤および六価クロムのスクリーニング法として有望と思われる。

近年, 測定基板に銀基板を用いた TOF-SIMS 法による樹脂の分子量分布や構造情報を得る方法が報告されている<sup>4-8)</sup>。銀原子を伴う擬似分子イオンが高感度で検出でき, 物質の構造情報を得るものである。

臭素系難燃剤は分子量が数百から数千におよぶものが多いため銀基板を測定基板とする方法の適用を検討した。銀基板上で樹脂から臭素系難燃剤を溶媒で簡易に抽出後, TOF-SIMS 測定する方法(一滴抽出法)を検討した結果, 臭素系難燃剤のスクリーニングに有効であり, またクロマトメッキ表面の六価クロム判定にも一滴抽出法を適用し良好な結果を得ている。RoHS 対象物質の有効なスクリーニング法である一滴抽出法を紹介する。

## 2. 実 験

## 2.1 TOF-SIMS 測定

TOF-SIMS 装置は, Physical Electronics (PHI) 社製 Model2100 TRIFT II を用いた。測定条件は以下の通りである。一次イオン:  $^{69}\text{Ga}^+$  (15 kV, 2 nA), 質量範囲:  $m/z = 1 \sim 1200$ , 質量分解能:  $\Delta M/M = 5000$ , ラスター領域:  $50 \mu\text{m}$  (臭素系難燃剤),  $100 \mu\text{m}$  (クロム)。定量分析を目的としてイオン強度値を得る場合は, 基板内を3箇所測定しその平均値を使用した。

## 2.2 試薬・試料

臭素系難燃剤の標準物質として, 次の試薬を用いた。デカブロモジフェニルエーテル (DeBDE) (和光純薬工業製1級試薬), オクタブロモジフェニルエーテル (OcBDE) (WELLINGTON LABORATORIES 社製  $50 \mu\text{L}/\text{mL}$  2,2', 3,3', 4,4', 6,6', -OcBDE 標準溶液), ペンタブロモジフェニルエーテル (PeBDE) (AccuStandard 社製  $50 \mu\text{L}/\text{mL}$  2,2', 4,4', 5-PeBDE 標準溶液), ポリ臭素化ジフェニルエーテル (PBB) (AccuStandard 社製  $100 \mu\text{L}/\text{mL}$  FiremasterBP-6 標準溶液), テトラブロモビスフェノール A (TBA) (帝人化成 FG-2000), テトラブロモビスフェノール A-ビス [2,3-ジブロモプロピルエーテル] (TBA-BP) (帝人化成 FG-

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表1 臭素系難燃剤の構造および分子量

Compound	Composition	Molecular Weight	Structure
Decabromodiphenylether (DeBDE)	C12OBr10	959.17	
2,2',3,3',4,4',6,6'-Octabromodiphenylether (OcBDE)	C12H2OBr8	801.38	
2,2',4,4',5-Pentabromodiphenylether (PeBDE)	C12H5OBr5	564.70	
Polybromobiphenyl (firemaster BP-6) (PBB)	C12Hm-1Brm (m=1~10)	627.60 (m=6) 706.49 (m=7) 785.38 (m=8)	
Tetrabromobisphenol-A (TBA)	C15H8O2Br4	543.90	
Tetrabromobisphenol-A-bis[2,3-dibromopropylether] (TBA-BP)	C21H20O2Br8	943.66	

3100)。表1にこれら臭素系難燃剤の構造および分子量を示す。

臭素系難燃剤の抽出試験用樹脂として、樹脂用混練機を用いて耐衝撃性ポリスチレン (PS)、またはポリプロピレン (PP) と DeBDE を混練して DeBDE 含有量が 0.01~10 wt % 濃度となる樹脂を調製した。

クロム標準試料として、硫酸第二クロム  $\text{Cr}_2(\text{SO}_4)_3$  (和光純薬工業製 特級試薬)、重クロム酸カリウム  $\text{K}_2(\text{Cr}_2\text{O}_7)$  (和光純薬工業製特級試薬) を用いた。

TOF-SIMS 測定用基板として、銀 (Ag) 基板 (ALDRICH 社製 99.99% 厚さ 0.125 mm) とシリコン (Si) 基板を用いた。測定基板は、15 mm × 15 mm に切断した後、溶媒で超音波洗浄し乾燥させて用いた。

### 2.3 標準物質のスペクトル測定

臭素系難燃剤は溶媒に溶解するか、標準溶液を濃縮して標準液を調製した。クロム標準試料は、水で希釈して標準液を調製した。標準物質のスペクトル測定は、試験液 10  $\mu\text{L}$  (臭素系難燃剤) または 50  $\mu\text{L}$  (クロム) をマイクロピペットで、基板に滴下して、乾燥させて調製した測定試料で行った。

### 2.4 測定基板上での樹脂中臭素系難燃剤の抽出液のスペクトル測定

樹脂中臭素系難燃剤の抽出は、次の手順で行った。試料片を基板のほぼ中心に配置した後、樹脂と基板の間に溶媒 10  $\mu\text{L}$  を滴下した。次いで、樹脂を配置した基板を、内部に抽出溶媒の揮発を抑制するために少量の溶媒を入れたガラス製密閉容器内に密閉し、10 分間放置した。その後、配置した樹脂をピンセットで取り除き、抽出液を乾燥させた基板表面をスペクトル測定した。

本操作の試料 1 個当りの所要時間は、試料片の準備に 3 分、測定基板上への試料片の配置および溶媒の滴下に 2 分、抽出時間 10 分、樹脂片除去および基板乾燥に 5 分、スペクトル測定に 15~40 分 (3 回測定) で、約 35~60 分間で

ある。

### 2.5 クロマトメッキ表面のクロム抽出液のスペクトル測定

金属材料表面のクロム抽出は、次の手順で行った。溶媒 50  $\mu\text{L}$  を滴下した基板表面上に、試料を配置して、放置した。その後、試料を取り除き、溶媒を乾燥させた基板表面をスペクトル測定した。

## 3. 結果と考察

### 3.1 樹脂中臭素系難燃剤の測定<sup>9)</sup>

#### 3.1.1 標準物質のスペクトル測定

DeBDE [MW = 959.17] の質量スペクトルを Si 基板と Ag 基板で比較した。検出した質量スペクトルは、構成元素の精密質量数および同位体の自然存在比の計算値と比較して同定した。Si 基板での正イオンの質量スペクトルでは Si 基板由来の  $\text{Si}^+$  イオンのみが、負イオンの質量スペクトルでは  $\text{Br}^-$  および  $\text{Br}_2^-$  イオンを検出したのみで、DeBDE に由来するイオンは検出されなかった。

図1に Ag 基板での正イオン測定の質量スペクトルを示す。Ag 原子を伴う DeBDE の擬似分子イオン ( $\text{DeBDE} + \text{Ag}^+$ ) [MW = 1067.04] が強く検出され、臭素が 2 個はずれた ( $(\text{DeBDE} - 2\text{Br}) + \text{Ag}^+$ ) [MW = 907.23] が弱く検出された。また Ag イオンを伴わない分子イオン  $\text{DeBDE}^+$  [MW = 959.17] や DeBDE から臭素が 2 個引き抜かれた ( $\text{DeBDE} - 2\text{Br})^+$  (MW = 799.36) も弱く検出された。DeBDE<sup>+</sup> に対する ( $\text{DeBDE} + \text{Ag}^+$ ) のピーク強度比は約 10 倍であった。図2に Ag 基板での負イオン測定の質量スペクトルを示す。 $\text{Br}^-$ ,  $\text{Br}_2^-$ ,  $\text{Br}_3^-$  および DeBDE が開裂した  $\text{C}_6\text{Br}_5\text{O}^-$  が強く検出され、Ag 原子を伴う  $\text{DeBDE}^-$ , ( $\text{DeBDE} + \text{Ag})^-$  および ( $(\text{DeBDE} - 2\text{Br}) + \text{Ag})^-$  が弱く検出された。正イオン測定で検出される擬似分子イオン ( $\text{DeBDE} + \text{Ag}^+$ ) は、分子の構造を反映しているため同定が容易であり、イオンピーク

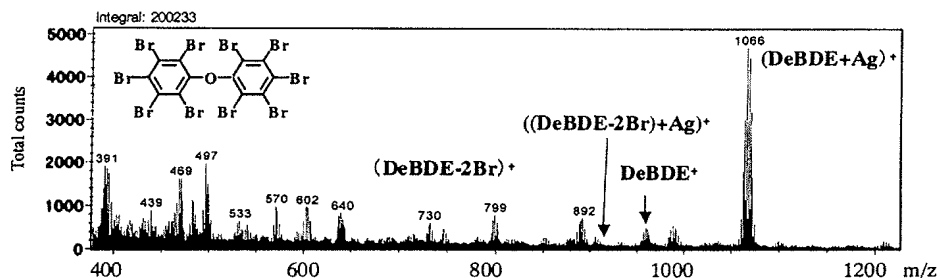


図1 DeBDE 標準試料の質量スペクトル (正イオン測定 Ag 基板)  $m/z = 400 \sim 1200$

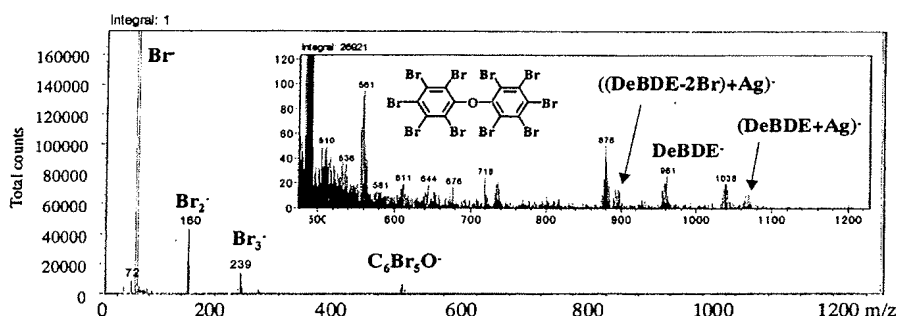


図2 DeBDE 標準試料の質量スペクトル (負イオン測定 Ag 基板)  $m/z = 1 \sim 1200$

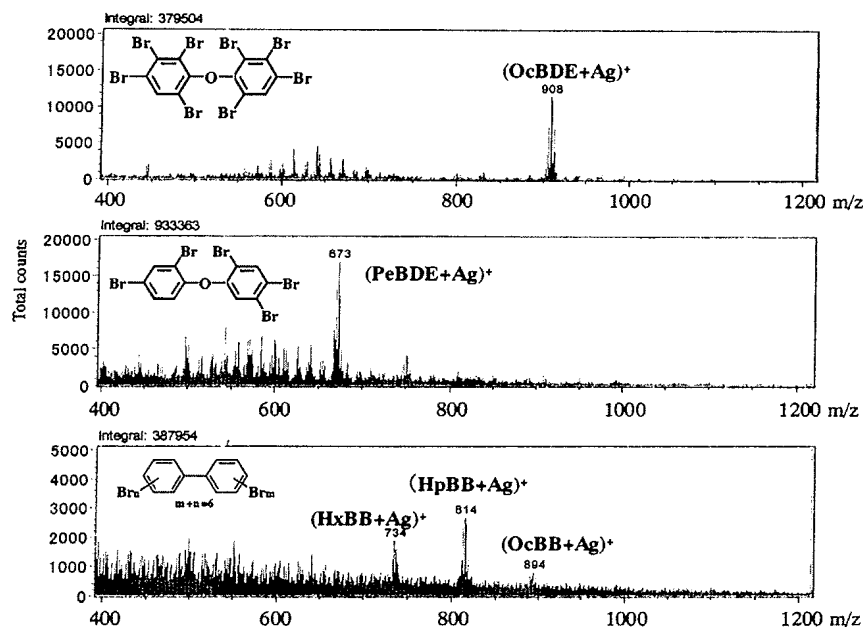


図3 OcBDE, PeBDE および PBB 標準試料の質量スペクトル (Ag 基板 正イオン測定)  $m/z = 400 \sim 1200$

強度が最も強いことから DeBDE の同定に最適であると判断できた。DeBDE のスペクトル測定は Ag 基板を使用した正イオン測定が適していることがわかった。

図3にPBDEの1種であるOcBDEおよびPeBDEとPBBの正イオン測定での質量スペクトルを示す。DeBDEと同様に銀を伴う擬似分子イオンである  $(\text{OcBDE} + \text{Ag})^+$  [MW = 909.25] および  $(\text{PeBDE} + \text{Ag})^+$  [MW = 672.57] が大きなイオンピーク強度で検出された。PBB 標準試料は臭

素数の異なる物質の混合物であるため、臭素数6~8のPBBの擬似分子イオン  $(\text{HxBB} + \text{Ag})^+$  [MW = 735.46],  $(\text{HpBB} + \text{Ag})^+$  [MW = 814.36] および  $(\text{OcBB} + \text{Ag})^+$  [MW = 893.25] が検出された。

PBDE および PBB の正イオン質量スペクトルでは、擬似分子イオン  $(\text{M} + \text{Ag})^+$  (M: 分子) の他に臭素が2個はずれた  $((\text{M} - 2\text{Br}) + \text{Ag})^+$  も弱く検出されるため、基本構造が同じで臭素数が2個少ない物質の質量スペクトルと一部



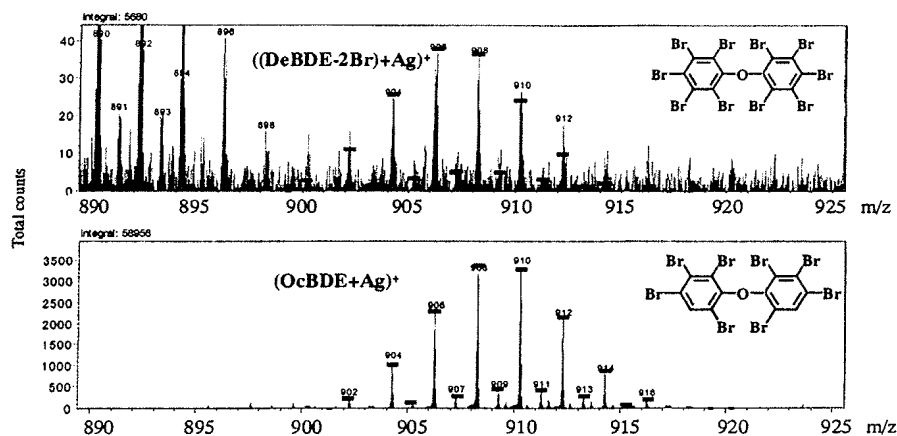


図4 DeBDE および OcBDE 標準試料の質量スペクトル (Ag 基板 正イオン測定)  $m/z=890\sim 925$

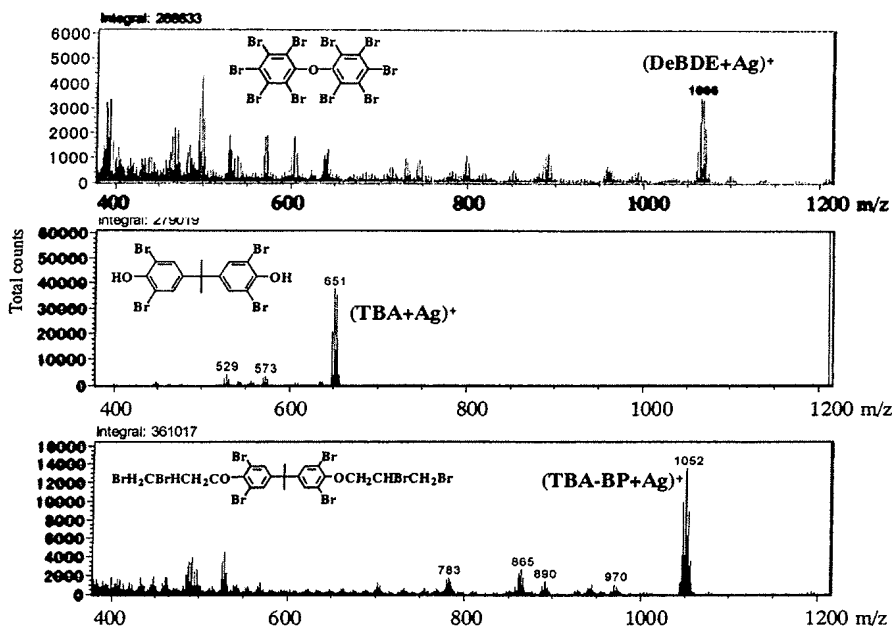


図5 TBA, TBA-BP および DeBDE 標準試料の質量スペクトル (Ag 基板 正イオン測定)  $m/z=400\sim 1200$

が重なる場合がある。例として、図4に  $m/z=890\sim 925$  の DeBDE と OcBDE の正イオン測定での質量スペクトルを示す。図中の横棒は、構成元素の同位体の質量数および自然存在比から計算したイオンピークの質量数と強度比を表している。((DeBDE-2Br)+Ag)+ と (OcBDE+Ag)+ は似た同位体パターンを持つが、((DeBDE-2Br)+Ag)+ は (OcBDE+Ag)+ より水素が2個少ない構造であるため、最も同位体存在比が大きなピークの質量数は異なる。計算された同位体パターンと良く一致したピークパターンが観測された。このように RoHS 指令で規制される臭素系難燃剤を区別して同定可能であることがわかった。

次に RoHS 指令で規制されない臭素系難燃剤の典型として TBA および TBA-BP を測定した。図5に TBA および TBA-BP の正イオン測定での質量スペクトルを示す。比較として DeBDE の質量スペクトルも示した。いずれの質量スペクトルにも Ag 原子を伴う擬似分子イオン (TBA+Ag)+

[MW = 651.76] および ((TBA-BP)+Ag)+ [MW = 1051.52] が確認された。これらの擬似分子イオンは、PBDE および PBB で検出される質量スペクトルとは質量数および同位体パターンが異なるため、判別が可能である。

### 3.1.2 測定基板上での樹脂中臭素系難燃剤の抽出液のスペクトル測定

DeBDE 濃度を0.01, 0.1, 1, 10 wt%に調製したポリスチレンおよびポリプロピレンの試料片を用いて、測定基板上での抽出およびスペクトル測定による定量性を検討した。

1 wt% DeBDE のポリスチレンの質量スペクトルを図6に示す。標準物質のスペクトル測定で得られた擬似分子イオン (DeBDE+Ag)+ と同じイオンが確認できた。質量範囲  $m/z=400\sim 800$  のスペクトルはポリスチレン樹脂本体や酸化防止剤などの他の添加剤に由来するものであるが、DeBDE のスペクトルへの妨害は認められなかった。0.01 wt% DeBDE のポリスチレンの質量スペクトルを図7に示す。(DeBDE+

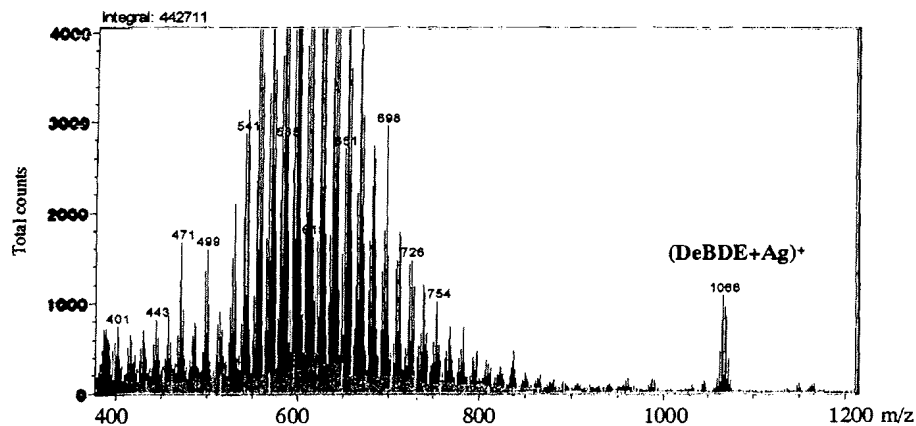


図6 1 wt%DeBDE ポリスチレンの質量スペクトル (Ag 基板上抽出物 正イオン測定)  $m/z=400\sim1200$

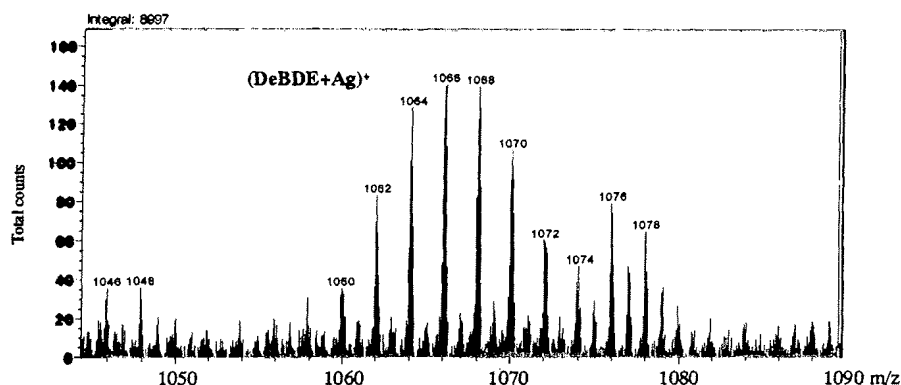


図7 0.01 wt%DeBDE ポリスチレンの質量スペクトル (Ag 基板上抽出物 正イオン測定)  $m/z=400\sim1200$

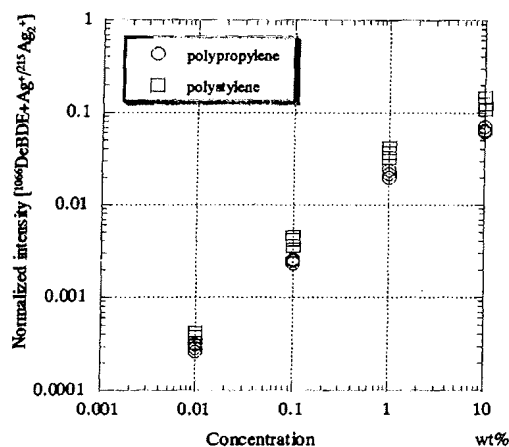


図8 樹脂中 DeBDE 濃度とピーク強度の関係

$\text{Ag}^+$  と同定できる同位体パターンを示す明瞭な質量スペクトルが得られた。ポリプロピレンの場合も同様な質量スペクトルが得られた。

ポリスチレンおよびポリプロピレン中の DeBDE 濃度とイオンピーク強度の関係を図 8 に示す。横軸は樹脂中の DeBDE 濃度 (wt%) であり、縦軸は規格化された擬似分子イオン  $(\text{DeBDE} + \text{Ag})^+$  のイオンピーク強度である。擬似

分子イオンのイオンピーク強度の規格化は、 $(\text{DeBDE} + \text{Ag})^+$  イオン強度と  $\text{Ag}^{2+}$  のピーク強度の比をとった。図中の各濃度における 3 点の検量点は、抽出操作を 3 回実施した結果である。ポリスチレンおよびポリプロピレンともに DeBDE 濃度が 0.01~10 wt% の範囲で、濃度の増加に伴ってイオンピーク強度が増加することがわかった。3 回測定結果にばらつきが認められるのは、抽出が試料表面のみでなされているために抽出効率が低いことが理由と思われる。

このように測定基板上での簡易な抽出法でも、樹脂中の DeBDE 濃度が 0.01~10 wt% の範囲で、濃度を見積もることが可能であることがわかった。

### 3.1.3 ガスクロマトグラフ質量分析法との比較

測定基板上での樹脂中臭素系難燃剤の抽出液のスペクトル測定による定量値とガスクロマトグラフ質量分析法の定量値を比較した。

評価試料は、家電リサイクル工場の樹脂分別工程の途中でサンプリングした樹脂破片 (ポリスチレンおよびポリプロピレン) である。樹脂破片を混練機で混合後、熱プレス機にて板状に成型した板を試料とした。ガスクロマトグラフ質量分析法による定量値で、DeBDE が 0.041~10 wt% 含む試料について測定基板上での樹脂中臭素系難燃剤の抽出液のスペクトル測定を行った。その結果を図 9 に示す。両法での定量値は良好な相関関係を示した。相関係数は  $r=0.976$  であっ

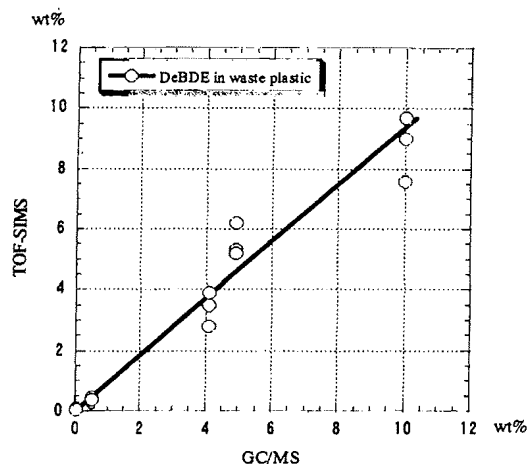


図9 GC/MS法とTOF-SIMSを用いた一滴抽出法の定量値比較

た。測定基板上での樹脂中臭素系難燃剤の抽出液のスペクトル測定により、家電製品に使用されている樹脂中の臭素系難燃剤の濃度評価が可能であることがわかった。

### 3.1.4 適用例

TOF-SIMS分析を用いる一滴抽出法を電気電子機器で用いられる部品に適用した例を示す。部品は、あらかじめエネルギー分散型蛍光X線分析を用いた元素分析で臭素の存在を確認した。図10はトランジスタ部品の被覆樹脂の質量スペクトルである。 $m/z=300\sim700$ に臭素を含むイオン種が検出されているがPBDEおよびPBBとは異なるものであることが判明した。また図11は高温条件で使用される両面テープ樹脂の測定結果である。質量スペクトルではDeBDE<sup>+</sup>が検出されており、DeBDEを含むことが明らかとなった。

## 3.2 クロメート処理表面の六価クロムの測定<sup>10)</sup>

### 3.2.1 標準物質のスペクトル測定

三価クロム(Cr(III))を含む硫酸第二クロムと六価クロム(Cr(VI))を含む重クロム酸カリウムのクロム標準試料を用いて、Si基板での正負イオン測定を行った。正イオン

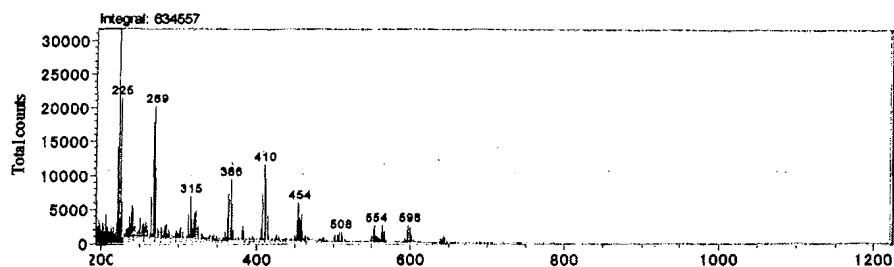


図10 トランジスタ被覆樹脂の質量スペクトル (Ag基板 正イオン測定)  $m/z=200\sim1200$

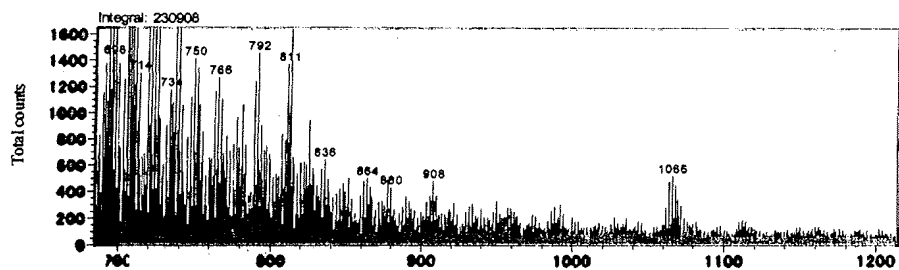


図11 両面テープ樹脂の質量スペクトル (Ag基板 正イオン測定)  $m/z=400\sim1200$

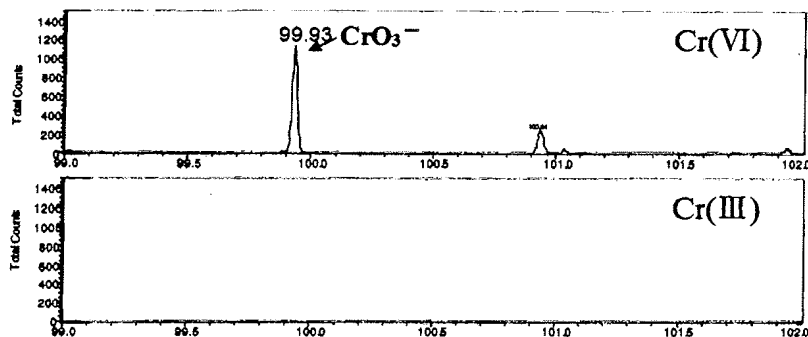


図12 クロム標準試料の質量スペクトル (Si基板 負イオン測定)  $m/z=99\sim102$

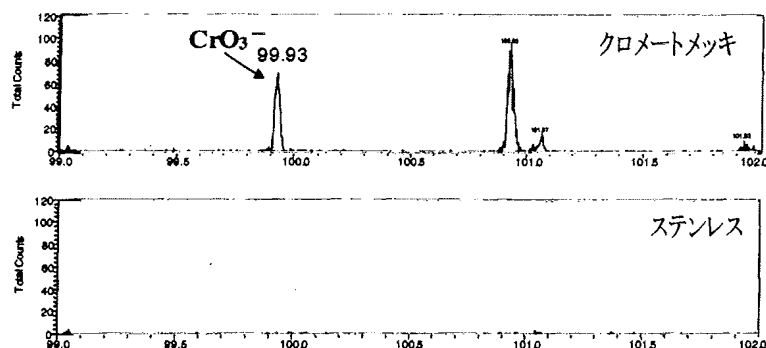


図13 市販ネジ材のクロメート処理表面およびステンレス表面の質量スペクトル（負イオン測定 Si 基板） $m/z=99\sim102$

測定ではCr(Ⅲ)およびCr(Ⅵ)ともに $\text{Cr}^+$  ( $m/z=51.90$ ) が検出された。負イオン測定（図12）では、Cr(Ⅵ)で $\text{CrO}_3^-$  ( $m/z=99.93$ ) が検出されたが、Cr(Ⅲ)では検出されなかった。 $\text{CrO}_3^-$  ( $m/z=99.9$ ) は近接の $\text{C}_3\text{H}_4^-$  ( $m/z=100.03$ ) と完全に分離して検出が可能であった。これより負イオン測定による $\text{CrO}_3^-$ の確認で、Cr(Ⅲ)とCr(Ⅵ)の判別が可能であることがわかった。クロム標準試料の濃度として $0.1\text{ }\mu\text{g/ml}$ まで検出可能であった。

### 3.2.2 市販ネジ材のクロメート処理表面の測定

市販ネジ材のクロメート処理表面のCr(Ⅵ)評価に一滴抽出法を適用した。比較としてステンレス表面も評価した。一滴抽出法により測定した質量スペクトルを図13に示す。

クロメート処理表面からは $\text{CrO}_3^-$ が検出されたが、ステンレス表面からは検出されなかった。このようにクロメート処理表面のCr(Ⅵ)の有無の判定に適用できることがわかった。

## 4. 結 論

樹脂中臭素系難燃剤濃度の評価方法として、銀基板上で抽出してToF-SIMS測定する方法（一滴抽出法）が有効であることを見出した。本法は樹脂中の臭素系難燃剤を同定することが可能であり、RoHS指令による規制対象物質のPBDE, PBBと規制対象外の物質を判別することができる。1試料の分析所要時間は35分～1時間であった。臭素系難燃剤濃度0.01～10 wt%範囲の濃度判定が可能であり、RoHS指令のしきい値（推定0.1 wt%）に対する判定が可能である。本法を廃プラスチックに適用した結果、定量値は既存分析法と良好な一致を得た。

またクロメート処理表面の六価クロム評価に一滴抽出法を応用した結果、 $\text{CrO}_3^-$ イオンの検出により六価クロムと三価クロムの判別が可能であることがわかった。

このように一滴抽出法は臭素系難燃剤および六価クロムの判定に有用であり、RoHS指令に係る規制物質のスクリーニング評価法として効果的といえる。

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## Rapid Screening Method for Brominated Flame Retardants and Hexavalent Chromium by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

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### Abstract

By Directive on RoHS<sup>[1]</sup>, the use of six hazardous substances is restricted to new electrical and electronic equipment put on the market in Europe from 1 July 2006. The estimation of the type and the content of brominated flame retardants is necessary in plastics of the equipment and the parts. The new technique by using time-of-flight secondary ion mass spectrometry (TOF-SIMS) is proposed for rapid screening test of these substances. We named this technique one droplet extraction method.

The sampling method of brominated flame retardants in plastic materials with toluene on silver substrate was investigated for analysis of trace organic compounds by TOF-SIMS. High impact polystyrene (PS) and polypropylene (PP) plates were prepared as evaluation samples containing Decabromodiphenylether (DeBDE) of 0.01-10wt%. Evaluation time that includes sample pretreatment time and measurement time was about 1 hour. The positive quasi-molecular ion (DeBDE+Ag)<sup>+</sup> (DeBDE cationized with Ag) was suitable for estimation of DeBDE. It was proved that content and spectral intensity had the clear magnitude correlation within 0.01-10wt% content of DeBDE.

It was found that the quick decision of whether the brominated flame retardants in the plastics is the substance restricted or not by Directive on RoHS is possible by this method. We can screen the substances in wide range of content of 0.01-10wt%.

Also it was found that the quick decision of whether hexavalent chromium is present in metals is possible by an application of this method.

It was confirmed that one droplet extraction method using TOF-SIMS is a very powerful technique for the rapid screening test of brominated flame retardants and Cr (VI). It can be expected that hazardous substance management that concerns Directive on RoHS becomes more reliable.

**Key words:** RoHS, brominated flame retardants, hexavalent chromium, mass spectrometry.

### 1. Introduction

By Directive on RoHS, the use of six hazardous substances (lead, cadmium, hexavalent chromium, mercury, and two brominated flame retardants (polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE)) is restricted to new electrical and electronic equipment (EEE) put on the market in Europe from 1 July 2006. Therefore we should exclude hazardous substances from EEES and control strictly. It is necessary to estimate materials and parts in EEES and to collect information of content of hazardous substances.

We require a screening method for estimating approximate content of hazardous substances in a short time. Although energy dispersion X-ray fluorescence spectrometry has become useful for element screening, it is difficult to distinguish hexavalent chromium (Cr (VI)) from trivalent chromium (Cr (III)) and it is impossible to identify the kind of brominated flame retardants. Although application of gas chromatography mass spectrometry is useful for the precise determination of trace brominated flame retardants<sup>[2]</sup>, this method generally needs a long time for sample preparation and measurement.

In contrast, TOF-SIMS is suitable for obtaining structural and quantitative information of trace organic and inorganic compounds in a relatively short time. Recently high sensitive detection methods by TOF-SIMS have been reported for various polymers on a silver substrate<sup>[3][4]</sup>. In addition, it is known that Cr (VI) gives a very strong peak of CrO<sub>3</sub><sup>-</sup> ion that is not seen well in the case of TOF-SIMS measurement of Cr (III)<sup>[5]</sup>.

We examined the ability of TOF-SIMS to estimate approximate content of brominated flame retardants in plastic materials<sup>[6]</sup> and Cr (VI) in metals. It was found that a sample preparation of extraction is effective to TOF-SIMS measurement and this method is useful for judgment of suitability of plastics and metals for Directive on RoHS. We named this method one droplet extraction method.

### 2. Experiment

Spectra of time of flight secondary ion mass spectrometry were obtained by using TOF-SIMS instrument (Model2100 TRIFTII, Physical Electronics (PHI), Inc.).

Extraction of brominated flame retardants from plastic materials on a silver substrate was done by the following procedures. First, a test piece was put on center of the substrate, and 10 $\mu$ L of toluene as solvent for extraction of brominated flame retardants was dropped on the test piece. Then, the substrate was put in a sealed glass chamber containing 1ml of toluene for 10 minutes in order to prevent vaporization of the solvent. The test piece was taken away by a pincer and the residue was air-dried. Extraction of Cr (VI) from metal surface on a silicon substrate was also done by the similar procedures except that an alkaline solution was used as solvent for extraction of Cr (VI).

TOF-SIMS spectra of extract of brominated flame retardants from plastic materials and Cr (VI) from metals were obtained from the surface of the substrate. The total time of procedures and measurement was about 35-60 minutes per one sample.

### 3. Results and discussion

#### 3.1. Brominated flame retardants

Figure 1 shows a positive TOF-SIMS spectrum of decabromodiphenylether (DeBDE) (MW=959.17) in the mass region  $m/z=0-1200$ . The intense peak in the mass region  $m/z=1050-1080$  corresponds to quasi-molecular ion cationized with  $Ag^+$ ,  $(DeBDE+Ag)^+$  (MW=1067.04), and the weak peak in the mass region  $m/z=900-920$  corresponds to  $((DeBDE-2Br)+Ag)^+$  (MW=907.23). It seems that  $((DeBDE-2Br)+Ag)^+$  was generated by abstraction reaction of two bromines from DeBDE and cationization with  $Ag^+$ . Peaks due to molecular ions cationized without  $Ag^+$ , shown as  $DeBDE^+$  (MW=959.17) and  $DeBDE-2Br^+$  (MW=799.36) in figure 1, are also observed. Peak intensity of  $DeBDE+Ag^+$  is about 10 times higher than that of  $DeBDE^+$  ion.

Figure 2 shows a negative TOF-SIMS spectrum of DeBDE in the mass region  $m/z=0-1200$ . The intense

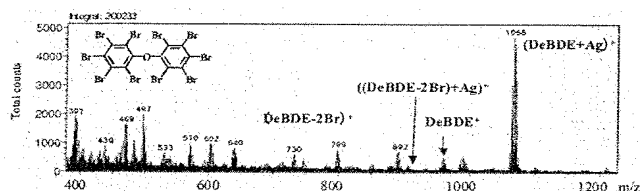


Figure1 Positive TOF-SIMS spectrum of DeBDE as standard reagent

peaks in the mass region  $m/z=1-300$  are due to  $Br^-$ ,  $Br_2^-$  and  $Br_3^-$ . In addition, there are four weak peaks;  $C_6Br_5O^-$ ,  $(DeBDE+Ag)^-$ ,  $((DeBDE-2Br)+Ag)^-$  and  $DeBDE^-$ .

It appears that quasi-molecular ion  $DeBDE+Ag^+$  shown in figure 1 is suitable for identification and

quantification of DeBDE, because peak intensity of this ion is the most intense and peak pattern of this ion reflects the molecular structure.

Figure 3 shows positive TOF-SIMS spectra of Octabromodiphenylether (OcBDE) (MW=801.38), Pentabromodiphenylether (PeBDE) (MW=564.70) and polybrominated biphenyls (PBB) in the mass region

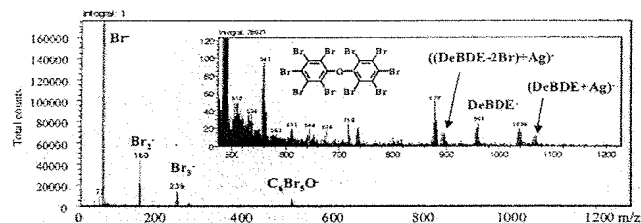


Figure2 Negative TOF-SIMS spectrum of DeBDE as standard reagent

$m/z=400-1200$ . The use of those compounds will also be restricted in electrical and electronic equipment. Intense peak due to quasi-molecular ion of  $(OcBDE+Ag)^+$  (MW=909.25) and  $(PeBDE+Ag)^+$  (MW=672.57) was observed respectively in the spectrum of OcBDE and that of PeBDE in a similar way to DeBDE in the positive spectrum. In the spectrum of firemasterBP-6 as PBB reagent, peaks of  $(HxBB+Ag)^+$  (MW=735.46),  $(HpBB+Ag)^+$  (MW=814.36) and  $(OcBB+Ag)^+$  (MW=893.25) were observed. PBB having the different number of bromine can be distinguished by the  $m/z$  number of quasi-molecular ion  $(M+Ag)^+$  (M: molecule).

Next we examined tetrabromobisphenol-A (TBA) and tetrabromobisphenol-A-bis [2,3-dibromopropylether]

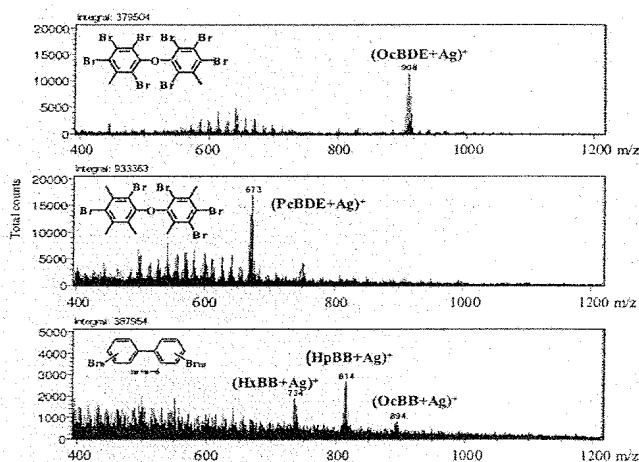


Figure3 Positive TOF-SIMS spectrum of OcBDE, PeBDE and PBB as standard reagent

(TBA-BP) as representatives of unrestricted brominated flame retardants by Directive on RoHS. Figure 5 shows

positive TOF-SIMS spectra of TBA (MW=543.90) and TBA-BP (MW=943.66) in the mass region  $m/z=400$ -1200 together with spectrum of DeBDE. Quasi-molecular ions with cationized  $\text{Ag}^+$ , shown as  $(\text{TBA}+\text{Ag})^+$  (MW=651.76) and  $(\text{TBA-BP}+\text{Ag})^+$  (MW=1051.52), were obtained and their  $m/z$  numbers differs from those of  $(\text{DeBDE}+\text{Ag})^+$ .

It was found that PBDE and PBB were distinguished from other brominated flame retardants by TOF-SIMS.

The relation between concentrations of DeBDE in plastic materials and peak intensities of  $(\text{DeBDE}+\text{Ag})^+$  was examined for standard resin samples containing 0.01, 0.1, 1 and 10wt% DeBDE on a silver substrate by one drop extraction method using TOF-SIMS.

Figure 6 shows positive TOF-SIMS spectrum of PS containing 1wt% DeBDE in the mass region  $m/z=400$ -1200. Quasi-molecular ions with cationized  $\text{Ag}^+$ , shown

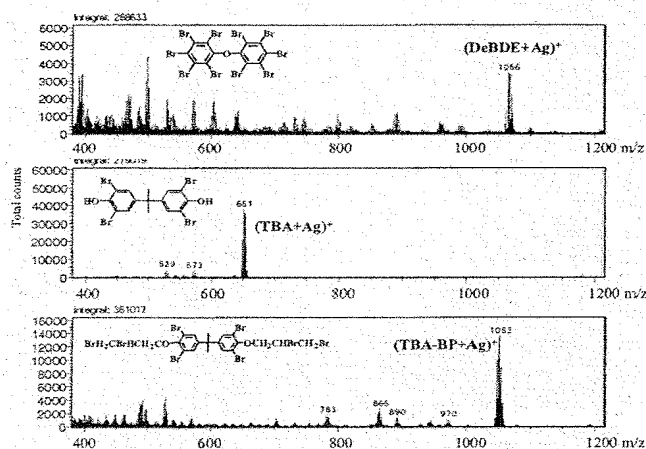


Figure4 Positive TOF-SIMS spectrum of DeBDE, TBA and TBA-BP in the mass region  $m/z=400$ -1200

as  $(\text{DeBDE}+\text{Ag})^+$ , was observed in the same way as observed in the positive spectrum of standard regent. Detection of  $(\text{DeBDE}+\text{Ag})^+$  was not interfered with fragment peaks in the mass region  $m/z=400$ -800, which derived from polystyrene resin and other additives (e.g., antioxidant, etc.). Figure 7 shows positive TOF-SIMS spectrum of PS containing 0.01wt% DeBDE in the mass region  $m/z=1040$ -1090. Clear peaks of  $(\text{DeBDE}+\text{Ag})^+$  were obtained. DeBDE in PP can be identified in the same method.

We plotted three data points of  $(\text{DeBDE}+\text{Ag})^+$  intensities normalized to  $\text{Ag}_2^+$  at each nominal concentration of DeBDE in figure.8. There is a clear

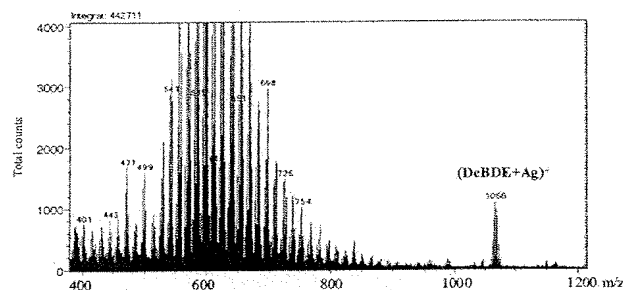


Figure5 Positive TOF-SIMS spectrum of PS containing 1wt% DeBDE

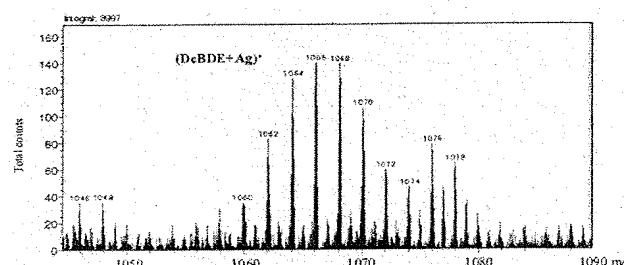


Figure6 Positive TOF-SIMS spectrum of PS containing 0.01wt% DeBDE

dependence of normalized intensities to nominal concentrations of  $(\text{DeBDE}+\text{Ag})^+$  in the range from 0.01wt% to 10wt%. Therefore, it was ensured that the concentration of DeBDE in plastic materials could be estimated by one droplet extraction method using TOF-SIMS over the range from 0.01wt% to 10wt%.

It is well known that GC/MS is the useful analytical method for the precise determination of brominated flame retardants. Each isomer of PBDE and PBB can be measured separately by this method. We compared the concentrations estimated by one droplet extraction method with those determined by usual analytical method using GC/MS.

Test resin samples were prepared by the following procedures. Pieces of plastic materials (PS or PP) in the course of plastics separation process at a recycling factory for electrical and electronic equipments were melted using a laboratory mixer with a heater and plates were made using hot-press equipment.

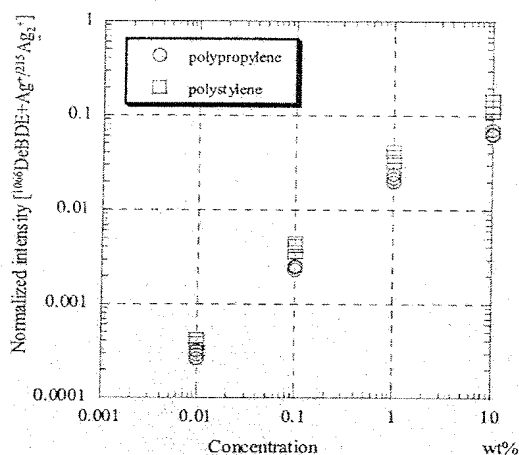


Figure7 Plots of normalized peak intensity of  $(\text{DeBDE}+\text{Ag})^+$  versus concentration of DeBDE in PS and PP

Test resin samples containing DeBDE as the concentration of 0.041-10wt% determined by GC/MS, were measured by one drop extraction method. Figure 9 shows the relation between the concentrations by one droplet extraction method and by GC/MS, where the former concentrations were estimated by utilizing the linear relationship between the normalized intensities by TOF-SIMS and nominal concentrations in figure.8. As shown in figure.9, an excellent correlation ( $r=0.976$ ) was observed between the concentrations by two methods.

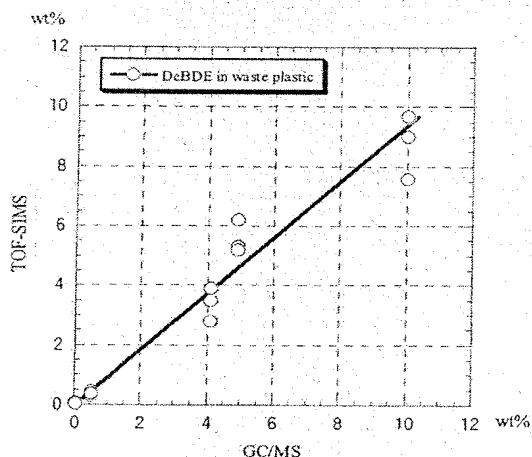


Figure8 Comparison between the concentrations estimated by one droplet extraction method and determined by GC/MS

Therefore, it was found that we could obtain the DeBDE concentration in plastic materials in a short time using one droplet extraction method.

### 3.2. Hexavalent chromium

Negative TOF-SIMS spectra of Cr (VI) and Cr (III) were compared by using test solution of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) and chromic sulfate ( $\text{Cr}_2(\text{SO}_4)_3$ ). Chromium oxide ion  $\text{CrO}_3^-$  was observed only in the spectrum of potassium dichromate containing Cr (VI). It was found that  $\text{CrO}_3^-$  was characteristic ion of Cr (VI). Figure 2 shows negative TOF-SIMS spectra of a stainless steel washer and a steel washer received a coating by hexavalent chromate treatment.  $\text{CrO}_3^-$  was observed only in the spectrum of a steel washer received a coating by hexavalent chromate treatment. Thus, it was found that it was effective as a method of screening Cr (VI).

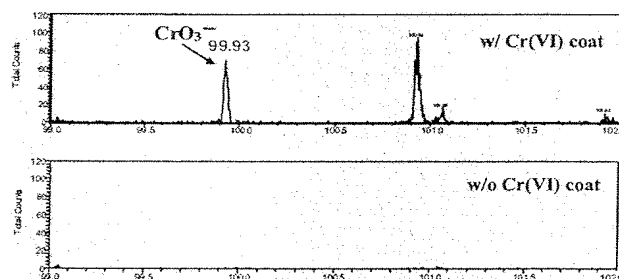


Figure7 Negative TOF-SIMS spectra of stainless washers

## 4. Conclusion

It was confirmed that one droplet extraction method using TOF-SIMS is a very powerful technique for the rapid screening test of DeBDE in plastic materials. We could identify the kind of brominated flame retardants, could distinguish the unrestricted compounds from the restricted ones by Directive on RoHS and could estimate the concentration of brominated flame retardants in the range of 0.01-10wt% by utilizing TOF-SIMS. It is concluded that we can judge whether the use of the specific plastics are allowed or not in electrical and electronic equipments in a relatively short time.

Also it was found that the quick decision of whether hexavalent chromium is present in metals is possible by an application of this method.

It was confirmed that one droplet extraction method using TOF-SIMS is a very powerful technique for the rapid screening test of brominated flame retardants and Cr (VI). It can be expected that hazardous substance



management that concerns Directive on RoSH becomes more reliable.

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# 有害物質の短時間分析手法

## 一滴抽出法による六価クロム、臭素系難燃剤の分析

三菱電機㈱ 黒川 博志

### はじめに

欧州でのRoHS指令により鉛、水銀、カドミウム、六価クロム、臭素系難燃剤(PBB、PBDE)の使用が制限される。これに対応するためには、製品構成材料の物質含有情報が不可欠となるが、この情報を最も確実に得る手段は分析である。6物質の含有情報を得るための分析技術として、蛍光X線が注目され、幅広く普及しつつあるが、蛍光X線で得られるのは元素情報のみであり、6物質中の六価クロム、臭素系難燃剤を特定することはできない。六価クロムに対してはジフェニルカルバジド吸光分析<sup>1)</sup>、臭素系難燃剤に対してはGC-MSによる分析手法<sup>2)</sup>があるが、これらは分析に長時間を要するため、RoHS指令対応として要求される多量の試料の分析には問題がある。ここではこの問題を解決するために開発した、TOF-SIMSを利用した一滴抽出法について述べる。一滴抽出法では六価クロム、臭素系難燃剤について100 ppm以下の検出感度で1時間以内での分析が可能である。

### 一滴抽出法

一滴抽出法とは、基本的にはTOF-SIMSによる高質量分解能での分析を利用して、化合物種を特定して高感度に分析する手法である。溶剤を一滴試料に滴下することにより抽出を行う前処理方法の特徴から一滴抽出法と名づけた。

一滴抽出法の分析フローは図1に示す通りである。基板(Ag)上に試料を置

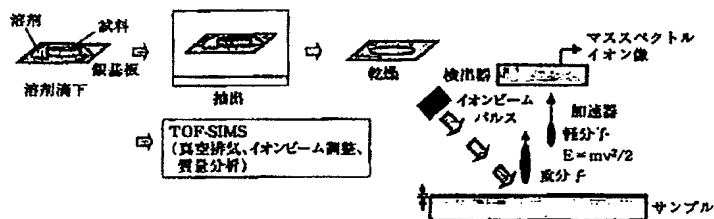


図1 一滴抽出法の分析フロー

き、この上に溶剤を少量滴下する。試料サイズによっては一滴の溶剤でも抽出可能であることから一滴抽出法と名づけた。滴下した溶剤に試料が触れている状態で5分程度放置することにより含有する難燃剤等を抽出する。抽出作業終了後は試料を取り除き、乾燥させてTOF-SIMSの測定を実施する。非常に単純な手法であるが、これによりRoHS指令で規制対象となる難燃剤2種の分析が可能である。

#### (1) 一滴抽出法による難燃剤(PBDE)の分析

DeBDEと呼ばれる10個のBrを有するPBDEの分子構造は、図2に示す通りである。一滴抽出法ではAg基板上に抽出して、これを試料としてTOF-SIMSの測定するため、Br、Agの同位体を考慮すると表1に示す質量数のピークが検出される。ここに挙げたものはTOF-SIMS測定のイオン化の過程で分解されず、もとの構造をそのまま保ってイオン化したものであり、このようにもとの構造を保ってイオン化したものを用いることにより、

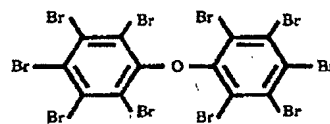


図2 DeBDEの分子構造

物質特定で間違いが生じないようにしている。DeBDEについて測定した質量スペクトルを図3に示すが、表1に示す質量数のピークが同位体の存在比を反映した強度比で検出されている。各ピークの強度比も物質特定の1つの指標として用いている。

図4にDeBDEと規制対象外であるTBA-BPおよびTBAの質量スペクトルを示すが、それぞれ全く異なるフラグメントパターンを示しており、一滴抽出法により明瞭にDeBDE等PBDEおよびPBBの検出が可能である。

#### (2) 一滴抽出法による六価クロムの分析

六価クロムを含む重クロム酸カリウムと三価クロムを含む第二硫酸クロムにつ

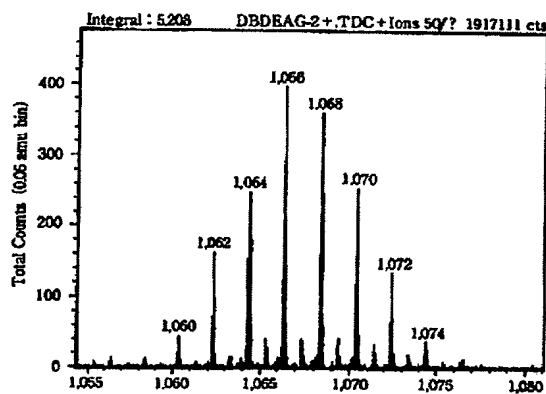


図3 DeBDEの質量スペクトル

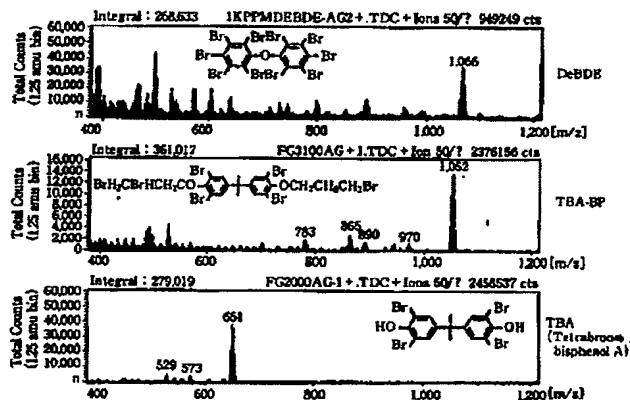


図4 種々難燃剤の質量スペクトル

表1 DeBDEのTOFSIMS測定で検出されるピーク

質量数	イオン種類 ( $^{12}\text{C}_x^{16}\text{O}^+$ )
1056	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$
1058	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{79}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1060	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{79}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1062	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{79}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1064	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{79}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1066	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{79}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1068	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{79}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1070	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{79}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1072	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{79}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1074	$^{79}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{79}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1076	$^{81}\text{Br}^{81}\text{Br}^{107}\text{Ag}$ , $^{81}\text{Br}^{81}\text{Br}^{109}\text{Ag}$
1078	$^{81}\text{Br}^{81}\text{Br}^{107}\text{Ag}$

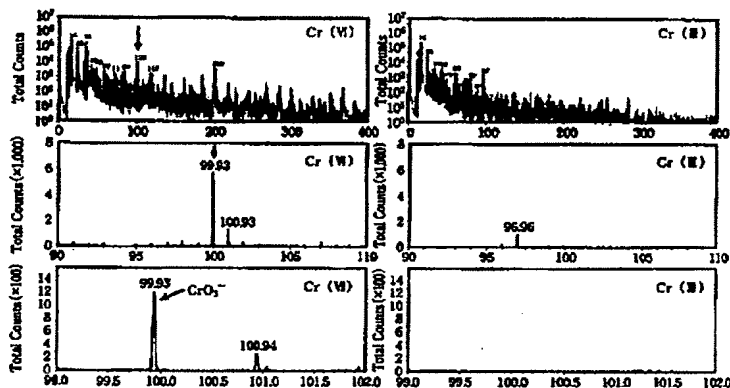


図5 六価クロム酸カリウム、第二硫酸クロムの質量スペクトル

いて測定した質量スペクトルを図5に示す。これより $\text{CrO}_4^{2-}$ イオンが六価クロムにおいてのみ検出されることがわかる。六価クロムの分析にはこの $\text{CrO}_4^{2-}$ イオンを利用する。

実際の例としてクロメート皮膜付きねじとステンレスワッシャーについて一滴抽出で測定した例を図6に示すが、 $\text{CrO}_4^{2-}$ イオンはクロメート皮膜においてのみ検出されており、ステンレスからは検出されていない。これにより六価クロムの分析が一滴抽出法により可能となることが確認された。

### (3) 一滴抽出法の特徴

RoHS指令に対応した分析技術とするためには、短時間で分析できることが必要である。一滴抽出法による分析時間と従来法（ジフェニルカルバジド吸光分析法、GC-MS法）をの分析時間比較を表2に示す。一滴抽出法で時間に幅を持たせているのは、必要感度により測定時間を調整するためであるが、いずれにしても、一滴抽出法では大幅な時間短縮が可能である。一滴抽出法の分析時間には、試料をTOF-SIMS装置に導入するため

の真空排気時間がかかなりの割合を占めるが、複数個同時に導入することが可能であり、実際上はさらに短時間での分析が可能であり、RoHS指令対応として数多くの試料を分析していくことが可能と考えられる。

一滴抽出法での測定感度について示す。PBDEを種々濃度で練りこんで作製した標準試料について測定した例を図7に示す。これより、一滴抽出法では100 ppmまで測定可能であることがわかる。RoHS指令におけるPBDEの閾値は、現

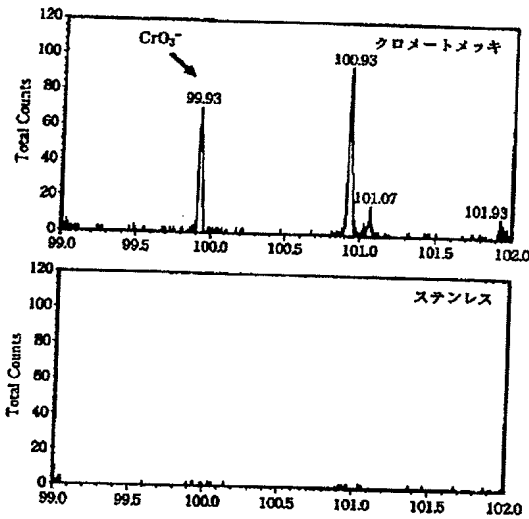


図6 クロメート皮膜付きねじ、ステンレスワッシャの一滴抽出法分析

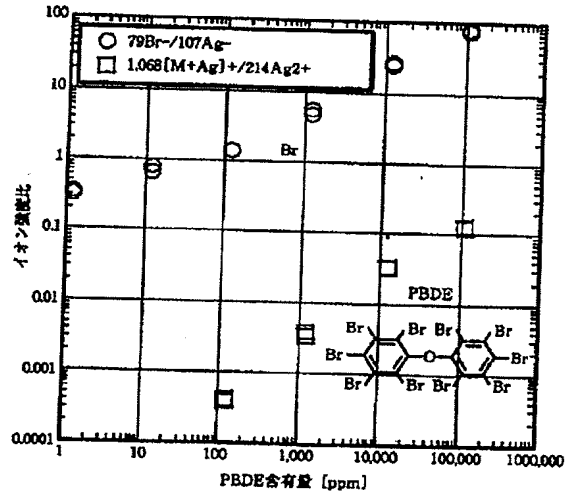


図7 一滴抽出法によるPBDEの検量線

表2 一滴抽出法と従来の分析時間比較

	一滴抽出法	従来法
6価クロム	35～60分	15時間
PBB, PBDE	35～60分	50時間

時点では決定されていないが、1,000 ppmに設定される可能性が高いと言われており、1,000ppmの閾値に対して100 ppmの検出感度を有することは含有量判定において十分な能力を有していると考えられる。精度について検証するため、GC-MSによる分析値との比較を行った。結果は図8に示す通りであるが、ある程度のばらつきは見られるものの両者の間に一定の相関関係が成立し、精度の点でも特に問題ないことが確認された。

六価クロムの検出感度であるが、クロメート皮膜という薄膜に含有されており、その濃度決定が難しいことから標準液による確認を実施した。図9に結果を示す通り0.01ppmまで検出可能であり、十分高い検出感度を有していると考えられる。ただ、これでは実試料に対して抽出効率を含めてどの程度のものかは判定しきれ

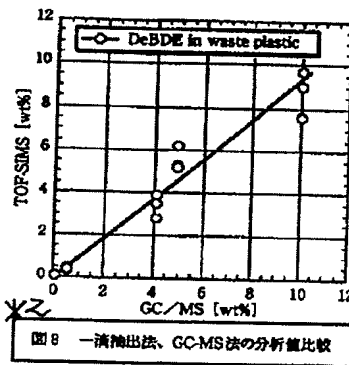


図8 一滴抽出法、GC-MS法の分析値比較

ていないと考えられるが、図10に例を示すように蛍光X線ですべてCrとしてほとんど検出されない試料に対しても、一滴抽出法では六価クロムを検出しており、この例を合わせて考えれば、六価クロムの分析に対しても十分な感度を有していると考えられる。

### ● 一滴抽出法の応用

一滴抽出法の応用例として図11に示す

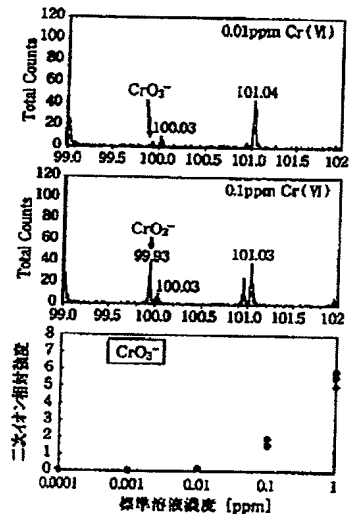


図9 六価クロム標準溶液とCrO<sub>3</sub><sup>-</sup>相対強度との関係

ような部品の測定例について示す。この部品に対しては、まず分析点1、2と示す部分について蛍光X線の測定を行っ

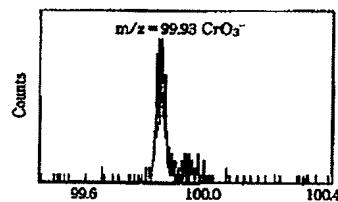
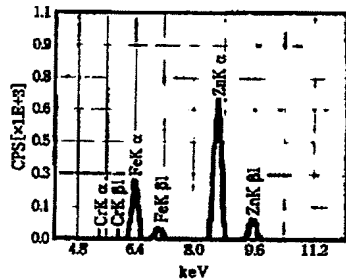


図10 Cr検出の蛍光X線と一滴抽出法の比較

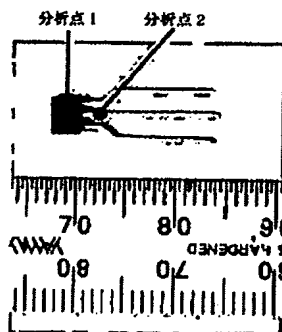


図11 評価対象部品

た。結果は図12に示す通りであるが、分析点1においてBrが検出されており、これが規制対象のPBB、PBDEであるかどうかの確認が必要である。分析点1について一滴抽出法により分析した結果を図13に示す。参考のためPBDEの測定結果を合わせて示すが、両者は明らかに異なるフラグメントパターンを示しており、規制対象のPBDEは含まれていないことがわかる。

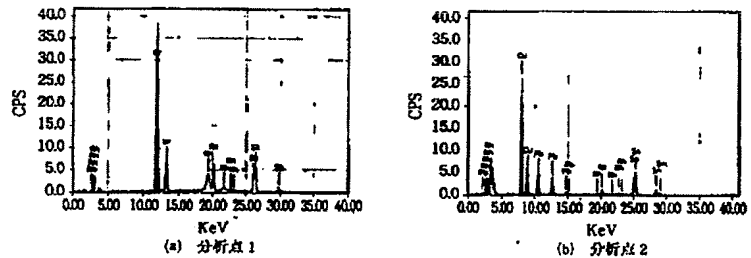


図12 分析点1,2の蛍光X線スペクトル

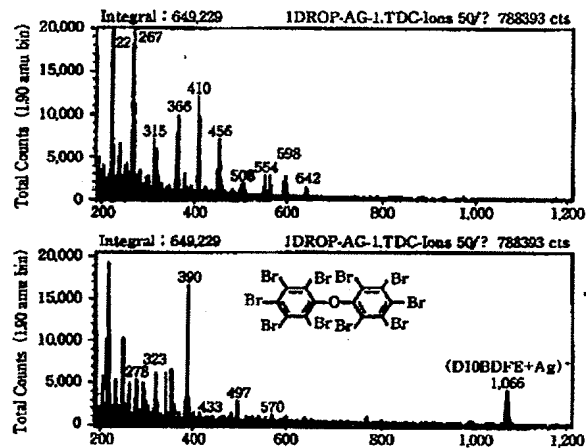


図13 分析点1の一滴抽出法分析

一滴抽出法はこのように蛍光X線でCr、Brが検出された場合にそれが六価クロムかどうか、PBB、PBDEであるかどうかの確認として用いている。この確認をジフェニルカルバジド吸光分析法、GC-MS法で行えば、長時間を要することになり、実際上は対応が困難な状況である。

## ● おわりに

RoHS指令の施行時期も近々に迫ってきて、部品等に含まれる規制対象物質の分析も数多くなっている。先にも述べたように蛍光X線でCr、Brが検出さ

れた場合の確認に一滴抽出法を利用しているが、Cr、Brが検出される部品もかなりの数にのぼり、一滴抽出法なしでは対応しきれない状況に至っている。一滴抽出法の普及には高額な装置が必要等の困難をともなう事情もあるが、それを乗り越えた今後の普及を期待したい。

## 【参考文献】

- (1) JIS K0102
- (2) EPA Method 1614 (Aug.2003 Draft)
- (3) V. Bietos et al.: Anal. Chem. 63 (1991) 1933
- (4) P. A. Zimmerman et al.: Appl.Spectrosc. 48 (1994) 620

(筆者紹介はP.79参照)

## Reference

\*1

The measurement sensitivity in the "one droplet extraction method" is described. A measurement example of standard samples which are made of PBDE (polybrominated diphenyl ether) kneaded in various concentrations is represented in Fig. 7. As represented in this figure, it is found that the measurement by the "one droplet extraction method" can be performed down to a concentration of 100 ppm. The threshold value for PBDE in the RoHS (restriction of hazardous substances) directive has not been determined at this time; however, because the value is said to be probably set at 1,000 ppm, the detection sensitivity of 100 ppm against the threshold value of 1,000 ppm can be considered to have enough performance for determining content amounts. In order to examine the accuracy, the values were compared with analytical values by the GC-MS (gas chromatography - mass spectrometry) method. The result is represented in Fig. 8, in which, although certain variations are found therein, a fair correlation is seen between them; accordingly, it is confirmed that there are no particular problems also from the viewpoint of the accuracy.

\*2

Fig. 8. Comparison of analytical values between one droplet extraction method and GC-MS method.

## DETAILED DESCRIPTION

### [Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the analytical method of the heavy metal containing the platinum group metals of a silicon wafer surface about the metallic contamination analytical method of a silicon wafer.

[0002]

[Description of the Prior Art] In the electronic industry field, reduction of contamination resulting from material or a manufacturing process has been important SUBJECT in connection with the miniaturization of a semiconductor device, and the densification. Especially heavy metal pollution must be eliminated as much as possible, in order to degrade the performance of a semiconductor device remarkably. And in order to solve this problem, very-high-sensitivity analysis of the silicon wafer surface for metallic contamination detection is needed.

[0003] Although the method of decomposing and collecting from acid (for example, references, such as JP,H11-37992,A), such as fluoric acid, was conventionally adopted as metallic contamination analysis of a silicon wafer surface, In acid, such as fluoric acid (HF), the decomposition and collection of the metal in which an ionization tendency is smaller than silicon is becoming difficult as metal, such as gold (Au) in which an ionization tendency is smaller than silicon, platinum (Pt), and copper (Cu), is used for a semiconductor device.

[0004] Big aqua regia of oxidizing power is used for the decomposition and collection liquid of the metallic contamination analysis by the metal in which an ionization tendency is smaller than the silicon of a silicon wafer surface (for example, references, such as JP,H5-218164,A and JP,H5-226443,A), and effect is achieved.

[0005]

[Problem to be solved by the invention] As mentioned above, although aqua regia was used as collecting liquid for analysis of the metal in which an ionization tendency is smaller than the silicon of a silicon wafer surface, the following problems were among the analytical method which uses this aqua regia.

(1) Since foaming by the spontaneous reaction of the aqua regia 4 is remarkable as shown in drawing 3, the air bubbles 5 stick for the surface of the silicon (Si) wafer 1, and the recovery rate of the metal in the part falls. Since the holding time of the air bubbles 5 has dispersion within the 1st page of a Si wafer, the recovery within a field will become uneven. For this reason, it cannot be said about analysis of the metal impurity adhering to Si wafer 1 that that analysis accuracy is enough.

(2) In the platinum group metals (Pt, Ir, Ru, etc.) which an ionization tendency is smaller than silicon and are hard to dissolve also in aqua regia, although it is necessary to make leaving times into a long time, In the case of aqua regia, degradation of the solution was remarkable, and needed to divide and carry out recovery operation to numbers of times, and the fall of the accuracy of measurement by recovery time and the increase in the amount of collecting liquid is brought about.

[0006] The accuracy of the heavy metal containing the platinum group metals which are the contaminated metals of a wafer surface of one of the main purposes of this invention is high,

and there is in providing the analytical method by which recovery time was short-time-ized.

[0007]

[Means for solving problem] This invention makes a silicon wafer surface contact with a drug solution, and dissolves and collects the qualities of a metal contaminant of this silicon wafer surface in this drug solution. It constitutes as a feature using the aqua regia which diluted said nature concentration of a metal contaminant in said drug solution with pure water as said drug solution in the metallic contamination analytical method of the silicon wafer surface which carries out a quantitative analysis.

[0008] In the above-mentioned composition of this invention, the rate of the 37 weight % chloride (HCl) of each ingredient of the aqua regia diluted with front pure water, 70 weight % nitric acid (HNO<sub>3</sub>), and pure water is expressed by a volume ratio by 3:1:x (however, x positive number of 2-8). If the value of x which shows the rate of pure water becomes smaller than 2, the natural decomposition of a drug solution and foaming will occur easily, and since the dissolution rate of platinum-group-metals metal will fall if x becomes larger than 8, x is maintained at the above-mentioned range.

[0009] When making said silicon wafer surface contact with said drug solution, by warming said drug solution, the dissolution of the contaminated metal of a silicon wafer surface can be promoted, and recovery time can be shortened. A desirable temperature of warming is 50-80 \*\*. If temperature exceeds 80 \*\*, the natural decomposition of a drug solution and foaming will occur easily, and if temperature becomes lower than 50 \*\*, the dissolution rate of platinum-group-metals metal will fall, and recovery time increases.

[0010] In this invention, when making said silicon wafer surface contact with said drug solution, there is an effect which raises the dissolution rate of the contaminated metal of a silicon wafer surface further by carrying out supersonic vibration of said drug solution or said silicon wafer.

[0011] Thus, using rare aqua regia for collecting liquid achieves the duty of suppressing foaming by the spontaneous reaction of collecting liquid, and suppressing uneven-ization of the recovery rate within the wafer surface by air bubbles. Also in the element which is hard to dissolve, carrying out heating temperature up increases the dissolution rate, and the recovery of it in a short time is attained.

[0012]

[Mode for carrying out the invention] Next, the metallic contamination analytical method of the silicon wafer surface of an embodiment of the invention is explained with reference to Drawings.

[0013] Drawing 1 is a sectional view of the equipment for explaining the metallic contamination analytical method of the silicon wafer surface of a 1st embodiment of this invention. The silicon wafer 1 to analyze on the trays 2 settled exactly, such as a product made of a fluoro-resin of a size, first, the 37 weight % chloride (HCl), The silicon (Si) wafer 1 is calmly carried so that \*\*\*\*\* may be put in and the surface may contact with this rare aqua regia 3 the dilution aqua regia solution (rare aqua regia) 3 mixed with nitric acid (HNO<sub>3</sub>) by the volume ratio 3:1:4 of pure water (H<sub>2</sub>O) 70weight %. For example, by analysis of a 6-inch wafer, it puts into the rare aqua regia 3 about 10-ml tray 2 with 5 ml and an 8-inch



wafer.

[0014]The silicon wafer 1 is removed for the silicon wafer 1 after indirect about 5-minute liquid to the rare aqua regia 3, and the rare aqua regia 3 is collected.

[0015]Next, evaporate to dryness using [ hot plate ] the solution of this collected rare aqua regia, and a liquid component is evaporated, The residue is remelted in the solution of a suitable constant-volume product, It analyzes by inductive-coupling type plasma mass analysis (ICP-MS:Inductively Coupled Plasma-Mass Spectrometry), atomic absorption analysis (AAS:Atomic Absorption Spectrometry), etc.

[0016]Below, the example actually applied to metallic contamination analysis of the silicon wafer surface is shown.

[0017]Two or more platinum contamination Si-wafer samples on which a  $1 \times 10^{12}$  atoms/cm<sup>2</sup> grade etc. spread platinum (Pt) and which were made to adhere were prepared for the 8-inch Si-wafer surface. 10 ml of rare aqua regia which mixed this sample at a rate of HCl(37 weight %):HNO<sub>3</sub>(70 weight %):H<sub>2</sub>O=3:1:4 as shown in drawing 1 is thrown in in a tray, and on it, the field which a wafer analyzes is turned down and carried calmly. The wafer was removed after neglect for 5 minutes in the state, and the remaining rare aqua regia was collected.

[0018]As a conventional example, the aqua regia used at the time of recovery operation was not diluted, but it was got blocked and same recovery operation was also performed using dark aqua regia [ comparatively / (volume ratio) ] of HCl:70 weight % HNO<sub>3</sub>:H<sub>2</sub>O=3:1:0 37weight %. After evaporating to dryness after such recovery operation using the hot plate and remelting to a constant-volume product at 0.5 ml of 1 weight % HNO<sub>3</sub>, the solution was analyzed by ICP-MS.

[0019]As a result, in the method of this invention, platinum of average value  $=1.18 \times 10^{12}$  atoms/cm<sup>2</sup> and dispersion  $3\sigma=0.10 \times 10^{12}$  atoms/cm<sup>2</sup> (the ten numbers of samples) was detected. On the other hand, in the conventional method, they were average value  $=1.02 \times 10^{12}$  atoms/cm<sup>2</sup> and  $3\sigma=0.45 \times 10^{12}$  atoms/cm<sup>2</sup> (the ten numbers of samples).

[0020]Thus, by using the method of this invention shows that the result where measurement dispersion was stabilized few is obtained. By comparing average value shows that the recovery amount is also improving compared with the conventional method.

[0021]In this invention, since rare aqua regia is used for the collecting liquid for carrying out dissolution recovery of the metal impurity, foaming by the spontaneous reaction of collecting liquid decreases. Therefore, the effect that uneven-ization within a wafer surface of the recovery rate of a metal impurity by air bubbles like [ at the time of using the aqua regia (dark aqua regia) which has not been diluted ] is suppressed is brought about, and a recovery rate also improves further.

[0022]the above-mentioned embodiment -- pure water at the time of rare aqua regia creation (H<sub>2</sub>O) -- although x was comparatively set to 4, same effect will be acquired if it is a value of  $x=2-8$ . Neither the amount of collecting liquid nor leaving times at the time of recovery are also limited to a value of the above-mentioned embodiment.

[0023]A solution for remelting is not limited to these, although mixture of pure water, aqua regia,  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{H}_2\text{O}_2$ , etc. are raised.

[0024]Next, metallic contamination analytical method of a silicon wafer surface of a 2nd embodiment of this invention is explained. Although rare aqua regia was not warmed in a 1st above-mentioned embodiment, temperature-up heating of the rare aqua regia was carried out in this embodiment. Drawing 2 is a sectional view of equipment for explaining metallic contamination analytical method of a silicon wafer surface of a 2nd embodiment of this invention that processes a silicon wafer surface with warmed rare aqua regia. In this figure, temperature-up heating of the whole composition of drawing 1 is carried out using the hot plate 6.

[0025]Below, the example actually applied to metallic contamination analysis of the silicon wafer surface is shown.

[0026]Two or more samples on which a  $1 \times 10^{12}$  atoms/cm<sup>2</sup> grade etc. spread Pt and which were made to adhere are prepared for the 8-inch Si-wafer surface like a 1st above-mentioned embodiment, and the example of analysis of the amount of surface contamination by the method of this invention is shown.

[0027]In the case of the recovery operation at the time of pretreatment of Pt contamination analysis of this sample, as shown in drawing 2, 10 ml of rare aqua regia which mixed and prepared  $\text{HCl}$  (37 weight %),  $\text{HNO}_3$  (70 weight %), and  $\text{H}_2\text{O}$  (pure water) at a rate of 3:1:4 by the volume ratio is thrown in in a tray, and heating temperature up is carried out to every tray 75 \*\*. The field which a wafer analyzes on it is turned down, and is carried calmly, in the state, after fixed time neglect, it removes, and the remaining rare aqua regia is collected and a wafer is analyzed. The process from recovery to analysis is the same as that of a 1st above-mentioned embodiment.

[0028]Even when collection processing was performed in leaving-times 2 minutes, dispersion  $3\sigma = 0.12 \times 10^{12}$  atoms/cm<sup>2</sup> (ten numbers of samples) detection of was done, and average value  $= 1.16 \times 10^{12}$  atoms/cm<sup>2</sup>, and a last embodiment and a result practically equal of neglect during 5 minutes were obtained.

[0029]According to this embodiment, since temperature up is carried out at the time of dissolution recovery of a metal impurity and a dissolution rate rises, time to apply to recovery can be shortened.

[0030]According to a 2nd embodiment of the above, although temperature-up temperature at the time of recovery was 75 \*\*, an effect that at least 50-80 \*\* is the same is acquired. A heating method is not limited to what is depended on a hot plate. A solution comparatively for x, the amount of collecting liquid, and remelting of pure water at the time of rare aqua regia creation ( $\text{H}_2\text{O}$ ) can also apply the same conditions as a 1st embodiment of the above.

[0031]According to the above-mentioned embodiment, although platinum was explained as a contaminated metal of a silicon wafer surface, it is applicable also to analysis of heavy metals, such as other Ir(s) of platinum, Os, Ru, Rh, platinum-group-metals metallurgy of Pd, and copper. In the above-mentioned embodiment, recovery time of a contaminated metal can be shortened by carrying out supersonic vibration of a silicon wafer or the rare aqua regia.

[0032]

[Effect of the Invention]As explained above, the following effects can be acquired by the aqua regia which diluted the contaminated metal of the silicon wafer surface with this invention recovering, and analyzing.

- (1) When collecting contaminated metals from a silicon wafer surface, in order that collecting liquid may not foam, contaminated metals can be uniformly collected from a silicon surface, and the analysis accuracy of a contaminated metal improves.
- (2) The analysis accuracy of the concentration of contaminant of the platinum metal of a silicon wafer surface improves.
- (3) By heating the silicon wafer to analyze and the whole equipment containing collecting liquid, shortening of recovery time is possible.

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[Translation done.]